Energy Changes Involved in the Dilution of Zinc and Cadmium Amalgams

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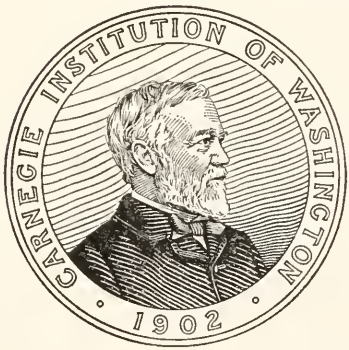

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ENERGY CHANGES INVOLVED IN THE DILUTION OF ZINC AND CADMIUM AMALGAMS.

By Theodore William Richards and George Shannon Forbes.

INTRODUCTION.

Nearly half a century ago a French physicist named Gaugain published a note[1] on his investigation of a voltaic pile whose "negative metal" was a dilute amalgam of zinc or cadmium. At first the electromotive force rose very rapidly when the proportion of oxidizable metal was increased, but beyond a certain point the introduction of fresh quantities of zinc caused no further variation. He concluded that these phenomena were occasioned by the affinity of the mercury for the amalgamated metal, an affinity which varied with the proportions of the amalgam. He also found that cadmium always had an electromotive force greater than its amalgams, no matter whether these contained cadmium in mere traces or in sufficient quantities to form a solid compound.

Shortly after, M. E. Becquerel[2] published an exhaustive and scholarly treatise on the "Disengagement of electricity in voltaic piles." His experimental skill and his logical interpretation of results appear remarkable when we consider the limitations of exact knowledge at that time. In this paper he suggested the probable existence of an approximate relation between the heats of combustion of different metals and their electromotive forces, and pointed out the importance of further work in this direction. Among the many substances examined by him were amalgams of zinc, manganese, ammonium, barium, calcium, sodium, and potassium. The dependence of electromotive force upon concentration was noted over a wide range, but no attempt was made to explain it. Very little improvement in the experimental or theoretical treatment of amalgams was made for thirty years after the publication of this work.

In 1863 Crova[3] concluded that amalgams containing from 1 to 5 per cent of zinc could be substituted for the zinc in a Daniell cell without change of

[1] Comptes Rendus, 42, 430 (1856).
[2] Ann. Chem. Phys., 48, 266 (1856).
[3] *Ibid.*, 68, 458 (1863).

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electromotive force. When the proportion of zinc was reduced to four-tenths of 1 per cent the electromotive force sank to nine-tenths of its original value. It is interesting to note that he considered the phenomena observed by Gaugain as quite analogous to the decrease of electromotive force in a cell, due to polarization.

In 1879 Hockin and Taylor[4] made extended observations on the electrical behavior of solid and liquid amalgams. Unfortunately their original paper is inaccessible. Their work, however, does not seem to have extended appreciably the theoretical knowledge of these concentration effects.

Three years later Helmholtz[5] published his masterly paper on the "Galvanic current caused by differences in concentration." The relation between the vapor tensions over two different aqueous solutions of a given electrolyte was made the basis for the calculation of the electromotive force between them. It was also pointed out that the latter should vary as the absolute temperature. Measurements on cells of copper sulphate and of zinc sulphate were in good agreement with the predicted values.

Elements consisting of concentrated amalgam as one electrode, and dilute amalgam as the other, with an interposed solution of metallic salt, although analogous to aqueous concentration cells, appear to have been altogether disregarded up to this time, and, in fact, for eight years after it. Gaugain, Becquerel, and the others had all aimed to improve the galvanic cell as a practical source of electricity. So when they attempted to explain the peculiar behavior of amalgams they always considered these separately in their relation to copper, platinum, zinc, or pure mercury, and never in relation to each other. Naturally little progress could be made by such considerations.

In 1888 Lindeck determined the potential of various amalgams of zinc, cadmium, lead, tin, and silver against amalgamated zinc in zinc sulphate solution. His measurements on zinc and silver amalgams are the most important. A part of them are given below.

(1) *Zinc amalgams.*

Per cent of zinc.	E. M. F.	Per cent of zinc.	E. M. F.
1.860	0.003	0.0010	0.11
0.467	0.022	0.00038	0.13
0.064	0.047	0.00027	0.14
0.028	0.057	0.00020	0.15
0.0014	0.096	0.00015	0.16

(2) *Silver amalgams.*

Per cent of silver.	E. M. F.
Saturated.	1.32
2.0	1.30
0.57	1.33

[4] Journ. Soc. Tal., 8, 282 (1879). "The Voltaic Cell," by Park Benjamin, pp. 148-151.
[5] Abstract, Chem. Cent. Blatt, [3] 13, 648 (1882).

It may be remarked in passing that the difference between any two electromotive forces in the first table would give at once the potential of a concentration cell containing the two corresponding amalgams.

In his theoretical discussion Lindeck calls attention to the fact that the metal silver behaves like mercury from an electrochemical standpoint.

The following year Ramsay[6] determined the molecular weights of almost all known metals by measurement of the vapor tension of mercury over their amalgams. In general the results were in agreement with the accepted atomic weights of the various metals. Sodium and calcium, however, appeared unmistakably smaller, suggesting the subdivision of their atoms, and causing anxiety among some upholders of the atomic theory.

In this same year Nernst published his well-known fundamental paper on "Die Electromotorische Wirksamkeit der Ionen." This paper did not dwell upon amalgam cells in particular,[7] but its application thereto is manifest.

In April, 1890, von Türin[8] published a complete theory of amalgam concentration cells, as a possible means of determining the molecular weights of the metals. He first considered a cell of the type

Mercury, Mercuric salt, Amalgam of "noble" metal.

Applying the osmotic theory developed three years before by van't Hoff,[9] he concluded that the electromotive force E was given by the equation $E = 1.728 \times 10^{-4} \left(\frac{n}{V}\right) \frac{T}{273}$ when T is the absolute temperature and $\frac{n}{V}$ the number of kilogram molecules of the metal in a cubic meter of mercury.

The cell of the type

Zinc amalgam concentrated, Zinc sulphate, Zinc amalgam dilute,

required different mathematical treatment. Pointing out the analogy between such an element and the cells investigated by Helmholtz, he decided that

$$E = 9.5636 \times 10^5 \, Tqk \log \frac{c_2}{c_1}$$

where q is the electrochemical equivalent for zinc, k the ratio between the molecular weights of mercury and zinc, and $\frac{c_2}{c_1}$ the concentration ratio of the amalgams. The paper, while very able, is somewhat marred by various minor errors, and contains no experimental data to support the formulæ

[6] Journ. Chem. Soc., 55, 521 (1889).
[7] Zeit. Phys. Chem., 4, 129 (1889).
[8] Zeit. Phys. Chem., 5, 340 (1890).
[9] Zeit. Phys. Chem., 1, 481 (1887).

deduced. It clearly establishes the priority of von Türin in announcing a consistent theory for amalgam cells, although it is probable that G. Meyer had already worked out much of it independently.

In May, 1890, Meyer[10] published a research on "The electromotive forces between glass and amalgams." Working at high temperatures the glass behaved as an electrolyte, and he was able to measure cells of the type

Mercury, Glass, Sodium amalgam.

By subtraction of the potentials of two cells containing amalgams of different concentrations, he calculated the potential of several cells of the type

Sodium amalgam dilute, Glass, Sodium amalgam concentrated.

He showed the process taking place in such an element to be reversible, and pointed out that the electromotive force should be proportional to the absolute temperature in case the heat of dilution was negligible. But his attempt to apply the principles laid down by Helmholtz was incomplete, and, so far as it went, discordant with his results. In a postscript to this article, however, he mentioned the article of von Türin, and stated that he had been for two months past occupied in determining the molecular weights of zinc and cadmium in mercury by a very similar method. These both corresponded with their atomic weights, and further investigation was in progress.

In November of the same year, von Türin,[11] in an address before the Russian Physico-Chemical Society, proved that his theoretical conclusions were verified by the measurements of Lindeck. He showed that all the metals investigated in that research were monatomic, and pointed out the bearing of Ramsay's experiments[12] upon the question at issue. No review of this address appeared in any German periodical at the time. In February, 1891, von Türin[13] corrected and amplified his first paper, but said nothing about the work of Lindeck.

Three months later G. Meyer[14] published his well-known research on the "Molecular weights of some metals," and reiterated his claim to priority in confirming the theoretical formula by experiment. He then developed the equation for zinc amalgam cells from a consideration of the osmotic work involved in a reversible cycle—a more direct treatment than von Türin's.

In the formula $E = 1.908 \frac{q}{m} T \log \frac{c_1}{c_2}$, q represents the electrochemical equivalent, in grams, of the metal, and m the molecular weight of the metal

[10] Wied. Ann., **40**, 244 (1890).
[11] Zeit. Phys. Chem., **8**, 141 (1891).
[12] J. Chem. Soc., **55**, 521 (1889).
[13] Zeit. Phys. Chem., **7**, 221 (1891).
[14] *Ibid.*, 477 (1891).

in the amalgam. The electromotive force between dilute amalgams of zinc, cadmium, lead, tin, copper, and sodium were measured with a fair degree of accuracy. The conclusion that these metals, including sodium, were monatomic in mercurial solution appeared well founded. Referring to Ramsay's work on sodium, he speaks of his own failure to confirm it *at the low temperature prevailing in his research.*

Von Türin,[15] in commenting upon Meyer's paper, called attention to his address before the Russian Society, but he still failed to mention Meyer's preliminary announcement in Wiedemann's Annalen.

His oversight in this respect may account for his ill-founded claim to precedence in the experimental as well as the theoretical development of the subject.

The relation of the special equations of von Türin and Meyer to the general equation of Nernst, $E = \frac{RT}{\nu F} ln \frac{P}{p}$, is sufficiently evident without further comment.

Seven years of inactivity in this line of investigation followed, and the reason for the discrepancy between Meyer's and Ramsay's results on sodium were still unexplained.

In 1898 Schoellers[16] prepared various amalgams of sodium and barium electrolytically, compared them with normal electrodes, and determined their concentration analytically. From a pair of such measurements, on either metal, the electromotive force of the corresponding amalgam cell could be found by subtraction. This in each case agreed well with the potential demanded by the logarithmic formula, on the assumption sodium and barium were monatomic. This research, however, was crude and left the question at issue still unsettled.

In October, 1898, Richards and Lewis presented to the American Academy their research on zinc and cadmium amalgams. Accurate determinations of electromotive force showed that zinc amalgams so concentrated as 1 per cent, and cadmium amalgams of 3 per cent obeyed the laws of dilute solutions with considerable fidelity. Neither the concentration of the electrolyte nor the nature of its anion had any influence upon the results, and the potentials were strictly proportional to absolute temperature. The second and third of these points, though inferred from the derivation of the formula, had not previously been verified by experiment. More important still was

[15] Zeit. Phys. Chem., 8, 141 (1891).

[16] Chem. Cent. Blatt, 70, I, 16 (1899); Zeitschr. Electrochem., 5, 259 (1899).

a calculation of h, the heats of amalgamation of zinc and cadmium, from the temperature coefficient of cells of the type

Electrolytic zinc, Zinc sulphate, Zinc amalgam.

If the equation of Helmholtz is thrown into the form $E = T\frac{dE}{dT} + h$, h can be found by assuming that $\frac{dE}{dT}$ and h are nearly constant at all temperatures. The result for zinc agreed so well with Favre's[17] calorimetric determination that confidence was placed in the value proposed for cadmium.

Another significant paper was published by Cady[18] in December of the same year. Working with sodium and calcium amalgams (the former more concentrated than Meyer's), he obtained molecular weights for the two metals in striking agreement with Ramsay's results. He now measured Q, the heat of dilution of sodium amalgam, and found that its conversion into electrical energy would account for the abnormally high potential of the corresponding cell. In other words, Meyer's expression must be replaced, in such a case, by the formula

$$\nu EF = Q + RT \ln \frac{c_1}{c_2}.$$

Ramsay's value for sodium could be made normal upon the application of similar treatment. Cady also showed that the electromotive force between tin amalgams in potassic stannate, where tin is quadrivalent, is half that observed in stannous chloride. Lewis, in a paper published in the Proceedings of the American Academy (volume 35, 1899), independently arrived at the same equation by thermodynamic reasoning.

Cady's work prompted Trevor[19] to work out a complicated treatment of the temperature coefficient of amalgam cells. This paper is valuable from the standpoint of pure mathematics, but the experimental facts necessary to verify his assumptions are not within reach at present.

The next theoretical contribution was made by Haber,[20] who showed the necessity of applying a new correction to the calculated potential of sodium amalgam cells. If sodium dissolves in mercury with the formation of $NaHg_6$, the reversible cycle described by Meyer must be amplified by a fourth step—the reversible squeezing out of six mols of mercury from the

[17] Jahn. Grundriss der Elektrochemie, p. 8.

[18] Journ. Phys. Chem., 2, 551 (1898). Attention should be called to a correction afterwards made in Cady's paper, without which it is incomplete and erroneous in one feature. Journ. Phys. Chem., 3, 107 (1899).

[19] Journ. Phys. Chem., 3, 95 (1899).

[20] Zeit. Phys. Chem., 41, 399 (1902).

dilute amalgam, and its reversible assimilation by the concentrated. This consideration raises the calculated electromotive force somewhat, but Haber pointed out the fact that the correction is less than the probable experimental error of Meyer's results. The possible effect of this compound in causing abnormal osmotic pressures was not considered, and no new experimental evidence was offered. In closing he entered a plea for more accurate experimental work on concentration cells to verify his theoretical deductions.

The nature and electrical behavior of cadmium amalgams was the subject of a long and interesting paper by H. C. Bijl,[21] published in the same year. Herein he recounts his measurements of the cells

$$Hg, \quad Hg_2SO_4, \quad CdSO_4 \text{ solution}, \quad HgCd_x$$

and

$$Hg, \quad Hg_2SO_4, \quad CdSO_4 \text{ solution}, \quad Cd.$$

He constructed curves showing the effect of concentration and temperature upon normal cadmium elements; his potentials appeared to be definite within a tenth of a millivolt—very accurate work, considering the experimental difficulties presented by solid amalgams. He showed that in a heterogeneous equilibrium of liquid and solid cadmium amalgams both phases had the same electromotive force. Finally, he calculated various heats of amalgamation and heats of crystallization by the method of Richards and Lewis. Owing to the complexity of the phenomena observed, his treatment of results is necessarily empirical, and contributes little to the theoretical knowledge of concentration effects *per se.*

In 1903 Roozeboom and Van Heteren,[22] using the method of Richards and Lewis, fixed the heat of amalgamation of tin at 3,000 calories.

The subject received a comprehensive theoretical treatment from the standpoint of the Phase Rule in the same year by W. Reinders.[23]

The most recent work upon the subject is that of J. F. Spencer,[24] published after most of the present work was completed. This work is mainly interesting on account of the clever device used in preparing the amalgams; but Spencer did not strive to attain great accuracy.

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[21] Zeit. Phys. Chem., **41**, 641 (1902).
[22] Chem. Cent. Blatt, **74**, II, 866 (1903).
[23] Zeit. Phys. Chem., **42**, 225 (1903).
[24] Zeitschr. Elektrochem., **11**, 681 (1905).

THE AIM AND SCOPE OF THE PRESENT RESEARCH.

The preceding review outlines the present theory of amalgam cells. No part of this theory has yet been verified with the precision that our present knowledge of absolute units would justify. The exactness of the equation of Cady is still somewhat in doubt, and Haber's considerations as yet lack adequate experimental support. Far more pressing is a proof of the precision of the gas law at infinite dilution. This law is a cornerstone of modern thermodynamics, but its exact truth is inferred more from extrapolation and analogy than from experimental data. These and minor considerations prompted the inception of the present research.

To solve these problems at all completely, the electrical measurement should be accurate to one hundred thousandth of a volt, and the calorimetric determinations of the heats of dilution precise to an equivalent degree. With such data at hand a distinct advance can be made.

There seems to be no reason why the potential of a given concentration of *liquid* amalgam at constant temperature should not be perfectly definite when all secondary effects are excluded. On the other hand, most solids, by reason of their variable surface energy, do not give very sharply defined potentials, and so do not come within the province of this research.

Sodium amalgams, though striking in their peculiarities, are hard to prepare in a state of unquestionable purity, and they react vigorously with aqueous solutions. Unpublished work by Richards and Lewis in 1899 failed to reveal any inert electrolyte for use in the cell. The method of Reuter,[25] who used alcoholic solutions at —80°, is impracticable for accurate work. Hence, zinc and cadmium amalgams, which appear open to neither of these objections, are selected as best adapted to the requirements of the research. It is true that preliminary experiments by the method of Richards and Lewis seemed to indicate a slight reaction with aqueous sulphate solutions, even when these had previously stood in contact with another sample of amalgam. But this effect was finally referred to oxidation and carefully eliminated in a manner soon to be described.

[25] Chem. Cent. Blatt, **73**, II, 1290 (1902).

THE VALUES OF THE CONSTANTS.

To introduce the subject of potential measurement, the quantities determining π in the simple formula $\pi\nu F = RT\ln\frac{c_1}{c_2}$ may be discussed, with a view to discovering how closely the numerical values selected for them may be identified with absolute physical conceptions. In future the symbol π will be used instead of E to designate electromotive force, in accord with the more general modern usage.

By the derivation of the equation for monatomic metals, ν is the valence of the metallic ion in the electrolyte connecting the two amalgams. Cady's [26] results are consistent with this premise, within the limit of error of his experiments, for the two valences of tin. It is hard to imagine how the valence of the zinc or cadmium ion in a sulphate solution could be anything else but 2; therefore, in all calculations involving ν, this number will be used.

Richards and Heimrod [27] have corrected four of the best determinations of the electrochemical equivalent of silver for small chemical errors. The new values were practically identical, in spite of a great variety of methods for referring the strength of the current observed to absolute units. Guthe [28] has recently come to the same conclusion. Hence, great confidence is placed in the conclusion that 96,580 coulombs are associated with a gram equivalent of silver. Richards, Collins and Heimrod,[29] and Richards and Stull [30] have established the universality of Faraday's law upon a firmer basis than ever. Hence, the same value, $F = 96{,}580$, is used for a gram equivalent of zinc with reasonable certainty. This value is based upon the usually accepted value 107.93 for the atomic weight of silver, and must be diminished by 0.04 per cent if silver is taken as 107.89.

The constant R is defined as the quantity $\frac{PV}{T}$, expressed in mayers, for a gram molecule of a perfect gas at any temperature. The recent work of Daniel Berthelot [31] makes it probable that the value of V under 760.00 mm. at 45° of latitude on the sea level is 22.412 liters, and that 0° A = — 273.08° C. Therefore these values will be used in the computations concerning a perfect gas, realizing that an error of 0.1 per cent, while improbable, is still possible.

[26] Journ. Phys. Chem. **2**, 558 (1898).
[27] Proceedings of American Academy, **37**, 415 (1902).
[28] Physical Review, **19**, 138 (1904).
[29] Proceedings of American Academy, **35**, 123 (1899).
[30] *Ibid.*, **38**, 409 (1902).
[31] Daniel Berthelot, Trav. et Mem. du Bureau internat. des poids et Mesures, **13**, 113 (1903). Also Zeitschr. Electrochem., **10**, 621 (1904).

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Upon this basis the value of R is

$$R = \frac{76.00 \times 13.596 \times 980.6 \times 22{,}412}{273.08 \times 10{,}000{,}000} = 8.316 \text{ mayers.}$$

It should be noted that barometric height and the acceleration of gravity are quantities difficult to determine accurately, but they can hardly be in such serious doubt as V.

In applying the formula $\pi vF = RTln \frac{c_1}{c_2}$, the above value of R is multiplied by T, the temperature of the cell, referred to the hydrogen scale. Over that part of the scale used in the following work these readings are essentially comparable with the corresponding thermodynamical temperatures. Hence no uncertainty is occasioned by the introduction of this factor into the formula. The experimental determination of temperature within one one-hundredth of a degree would fix the value assigned to $\frac{T'}{T_0}$ within 1 part in 30,000. This is far greater accuracy than can be attained in the determination of the rest of the data from which π is calculated.

The most serious experimental uncertainty lies in the ratio $\frac{c_1}{c_2}$; this may be written as equal to $\frac{V_2}{V_1}$ if V_1 and V_2 are respective volumes occupied by a gram molecule of the dissolved metal in the two amalgams. No reference is made to the number of gram molecules of mercury involved in either case.

Since π, in volts, $= 0.029 \log \frac{c_1}{c_2}$ approximately, at 20°,

$$\pi = \frac{\log \frac{c_1}{c_2}}{34} \text{ volts.}$$

If the concentration ratio recorded for a given cell had been 0.1 per cent too small, the true value of π should have been found from the equation

$$\pi = \frac{\log 1.001 \frac{c_1}{c_2}}{34} = \frac{\log \frac{c_1}{c_2}}{34} + \frac{\log 1.001}{34}$$

Since $\log 1.001 = 0.00044$

$$\pi = \frac{\log \frac{c_1}{c_2}}{34} + 0.00001 \text{ volt.}$$

Hence the calculated value of π will be in error 0.00001 volt if the concentration ratio is 0.1 per cent in error. Some serious obstacles to the determination of the ratio with this degree of precision will now be considered.

THE DENSITY OF AMALGAMS.

Previous investigators appear to have mixed a weight, W, of amalgam of concentration c_1 with a weight nW of mercury to form a new amalgam of concentration, c_2, and written

$$\frac{c_1}{c_2} = n + 1.$$

This assumption is not permissible in accurate work, as is shown by the following investigation of the densities of zinc and cadmium amalgams.

The zinc used for this purpose was electrolyzed from the "chemically pure" zinc sulphate of commerce, in ammoniacal solution, and washed with dilute ammonia, distilled water, alcohol, and ether; it was dried in a vacuum desiccator over strong sulphuric acid, to absorb all the ether vapor. The mercury was shaken with strong sulphuric acid, and passed through a tower [32] containing dilute nitric acid. The materials were weighed out into a stoppered tube, covered with dilute sulphuric acid, and shaken until all the zinc was dissolved. The sulphuric acid was pipetted off, neutralized with ammonia, and its zinc content determined by titration [33] with a solution of $K_4Fe(CN)_6$, 1 cc. = 0.003 gram zinc. The proper correction was then applied to the weight of zinc taken.

The pycnometer was of the Sprengel type, as modified by Ostwald; [34] its capacity was 5 cc., and its tubes 1 mm. in diameter. It was treated with cleaning solution, and after washing thoroughly, dried with alcohol and ether, followed by suction. When all was ready, the amalgam was hastily dried with filter paper and drawn into the pycnometer; the resulting oxidation was too small to affect the density of the product. The pycnometer was hung in a large beaker of water at a fixed temperature for a quarter of an hour, after which the surplus amalgam was withdrawn through an exceedingly fine capillary and the glass was wiped with a clean cotton cloth

No.	Pycnometer empty.	Pycnometer at 20° filled to mark 1.	Weight of mercury at 20° to mark 1.	Pycnometer at 16° to mark 2.	Weight of mercury at 16° to mark 2.
1	7.135	75.042	67.908	.....	.....
2	7.135	75.051	67.916	.....	.....
3	7.135	75.058	67.923	.....	.....
4	7.135	.....	.....	75.132	67.997
5	7.135	.....	.....	75.116	67.981
	Average.....		67.915	.....	67.989

[32] Ostwald-Luther, Hand- und Hülfsbuch, p. 131 (Leipzig, 1902).
[33] de Koninck and Prost, Zeitschr. f. Angew. Chem., 1896, 460, 564.
[34] Ostwald-Luther, Hand- und Hülfsbuch, p. 142.

and weighed at once. Since it was hard to adjust the amalgam to the mark as described above, the length of the surplus mercury column was carefully measured, at times, and a correction applied to the observed weight. (One centimeter of mercury in the tube weighs 0.200 gram, the mean of two determinations.) Corrected data are given without comment in the table at the bottom of page 11.

The record of a typical determination follows:

(1) Weighing bottle + zinc	9.8685
(2) Weighing bottle + zinc	9.1822
Weight of zinc	0.686

$K_4Fe(CN)_6$ solution used = 1.85 cc. Therefore, 0.006 gram of zinc was dissolved by sulphuric acid, and must be subtracted.

Weight zinc in amalgam	0.680 gram
Weight mercury in amalgam	82.12 gram
	82.80

$$\text{Per cent zinc in amalgam} = \frac{0.680}{82.80} \times 100 = 0.821 \quad (t = 20°).$$

Weight of pycnometer and amalgam	74.685 to mark 1.
Weight of pycnometer	7.135
	67.550 to mark 1.

The absolute density of mercury at 20° is 13.545.[35]

∴ the density of the amalgam is

$$\frac{67.550}{67.915} \times 13.545 = 13.472+$$

The table of results follows. In the last three calculations the assumption is made that the coefficients of expansion of mercury and amalgam over 4° are sensibly the same.

Densities of Zinc Amalgams.

No.	Per cent of zinc in amalgam.	t_0	Weight amalgam in pycnometer.	Weight mercury in pycnometer to same mark at t_0.	Density of amalgam at 20°.
		°			
1	0.821	20	67.550	67.915	13.472
2	0.644	16.4	67.722	67.987	13.493
3	0.733	16.4	67.667	67.987	13.482
4	0.180	16.6	67.914	67.985	13.530

From these figures a curve can be constructed giving the density of any zinc amalgam between 0.821 per cent and pure mercury; some extrapolation would probably be safe also.

[35] Ostwald-Luther, Hand- und Hülfsbuch, p. 129.

The cadmium was electrolyzed from a strong acid solution of " chemically pure " cadmic sulphate; otherwise the procedure was similar to that described for zinc. The weight of cadmium dissolved in one experiment was found to be negligible for present purposes; hence in succeeding experiments the titration was omitted.

The table of results follows:

Densities of Cadmium Amalgams.

No.	Per cent of cadmium in amalgam.	t_0 of thermo-stat.	Weight amalgam in pycnometer.	Weight mercury to inner end of mark in pycnometer.	Density of amalgam at 20°.
		°			
1	1.48	20.0	67.518	67.961	13.456
2	0.74	20.0	67.743	67.961	13.503
3	0.37	20.0	67.870	67.961	13.527
4	2.39	20.0	67.257	67.961	13.405
5	2.97	20.0	67.084	67.961	13.370
6	2.35	20.0	67.262	67.961	13.406

Nos. 1, 2, and 3 were made by dilution of amalgams of twice their respective concentrations with an equal volume of mercury.

The density curves are shown in figure 1. The dotted lines show the average mixed density of the unamalgamated components calculated from the following figures:

$$\begin{aligned} \text{Density of zinc} &= 7.04 \\ \text{Density of cadmium} &= 8.55 \\ \text{Density of mercury} &= 13.545 \end{aligned}$$

Consider, for example, the calculation of this quantity for a 3 per cent amalgam of cadmium:

One hundred grams of the mixture contain 3 grams of cadmium and 97 grams of mercury..

$$\therefore \text{ volume} = \frac{3}{8.55} + \frac{97}{13.545} \text{ cc.} = 7.512 \text{ cc.}$$

$$\text{Average density} = \frac{100.00}{7.512} = 13.312.$$

These dotted curves are very nearly straight lines; from the portion of any ordinate cut off between the upper and the lower curve for either metal, it is easy to calculate the contraction which takes place during the formation of the corresponding amalgam. Later these contractions will be discussed in their relation to various energy changes occurring in amalgamation.

Attention is now called to the method of using the undotted actual curves in calculating concentration ratios.

Let w_1 be the weight of amalgam A_1, which is diluted with w_2 grams of mercury to form a new amalgam, A_2; the percentage composition of A_2 is now calculated; then the densities of A_1 and A_2 are found from the curve to be D_1 and D_2, respectively.

$$\frac{c_1}{c_2} = \frac{v_2}{v_1} = \frac{\frac{w_1 + w_2}{D_2}}{\frac{w_1}{D_1}} = \frac{w_1 + w_2}{w_1} \times \frac{D_1}{D_2}.$$

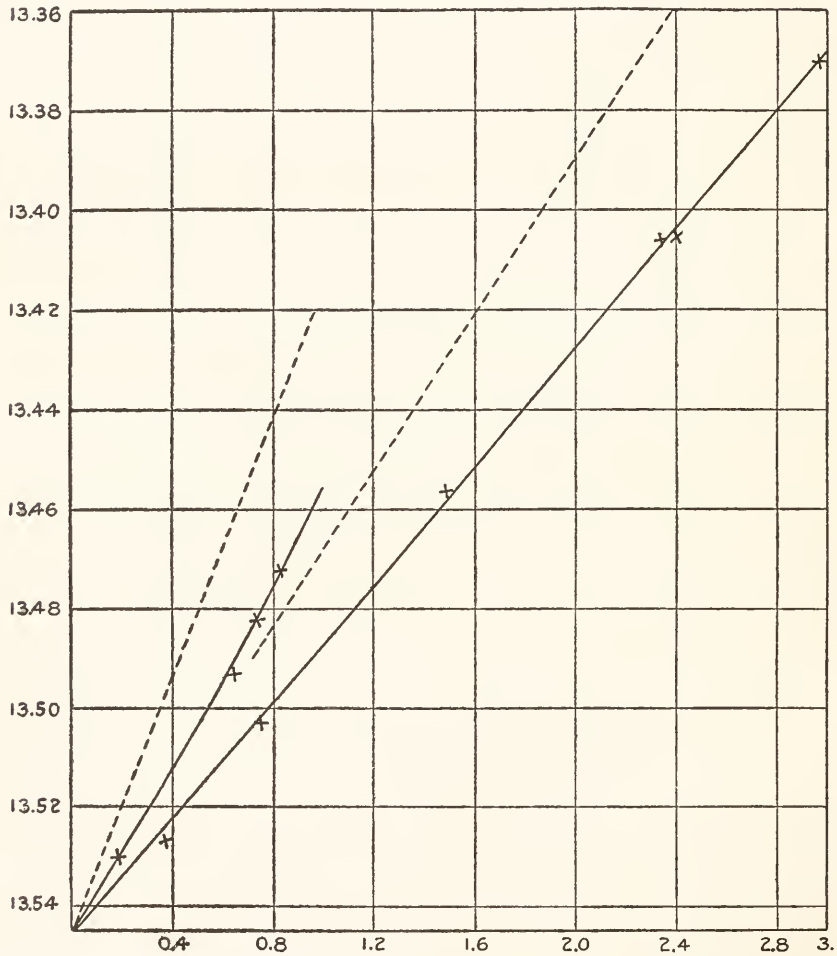

FIG. 1.—THE DENSITIES OF ZINC AND CADMIUM AMALGAMS.

Density is plotted ordinately; percentage composition in the direction of abscissæ. The shorter lines represent zinc; the longer, cadmium amalgams. The dotted lines give the theoretical values which would be observed if no contraction took place on mixing; the continuous lines give the actual values.

The factor $\frac{D_1}{D_2} = 0.995$ approximately when a zinc amalgam containing 0.9 per cent of zinc is diluted with nine times its weight of mercury; the same dilution of 3 per cent cadmium amalgam will introduce a factor of 0.987. Neglect of this consideration makes the calculated values for π too high in all cases, and the error may be a serious one.

THE PURITY OF THE MATERIALS.

All the materials used in potential work were purified with great care. "Chemically pure" zinc sulphate was dissolved in twice-distilled water to form a fairly strong solution. This was allowed to stand in Jena glass for a month over electrolytic zinc made from another sample of the same salt. Fresh portions of zinc were added every week, and the flasks were frequently shaken to bring all parts of the solution into contact with the metal. The last portion of zinc added was made from a salt prepared for atomic-weight work in this laboratory.[36] The product was filtered on pure filter papers and recrystallized three times in platinum. The feathery crystals obtained were each time separated from the mother liquor with great completeness by a small centrifugal[37] similar to those used in urine analysis. The efficiency of this device was so great that a cubic centimeter of liquid could easily be separated from three times that bulk of pressed crystals.

The final product was dried on a watch glass and used in the concentration cells without further treatment.

A generous supply of very pure cadmium sulphate prepared for atomic-weight work used was kindly placed at our disposal by Professor Baxter and Mr. Hines.[38] The sample in question had been twice precipitated as sulphide, dissolved in nitric acid, evaporated with excess of sulphuric acid, three times recrystallized, and dried at 100°. It was used for the concentration cells without further purification.

The double precipitation as sulphide must have excluded those metals, zinc especially, which could become sources of error in the later part of the work.

Crude mercury was shaken with sulphuric acid to remove the major part of its metallic impurities. Then it was vigorously shaken for a long time with a solution of mercurous nitrate and nitric acid prepared from a sample

[36] Richards & Rogers, Proc. Am. Acad., 31, 158 (1895). This treatment is important in order to separate any metal of less solution tension, which would later replace zinc in the amalgam and lower its electromotive force.

[37] Journ. Am. Chem. Soc., 27, 109 (1905).

[38] *Ibid.*, 222 (1905).

of mercury which had undergone a similar purification. According to Hulett,[39] the resulting product should be very pure. It was then distilled under 20 mm. of hydrogen in an apparatus suggested by Hulett, but improved by the elimination of rubber joints. The hydrogen generator used was similar to the one to be described on page 19. A long tube containing granulated calcium chloride dried the gas before it entered the mercury. All air was replaced by hydrogen as completely as possible before heating the mercury.

The entire apparatus was one continuous piece of blown glass without a single piece of cork or rubber, as far as the exhaust to the water pump. A stopcock regulating the supply of gas bubbling through the mercury was lubricated with sirupy phosphoric acid. The possibility of leakage of air or the introduction of sulphur compounds was thus eliminated. Great confidence was placed in the purity of the product.

The materials thus described contained no impurities dangerous to the success of the potential measurements. In fact, as there was to be measured only a concentration effect, it seemed highly probable that pure materials of commerce would have done almost as well. A few approximate experiments, performed after the work with pure materials was finished, tended to bear out the truth of this supposition. Nevertheless, it was desired to run no risks, and complete purity was therefore sought, as far as possible.

Water twice distilled in a block-tin condenser was used to prepare all solutions. All vessels used in this part of the research were treated with cleaning solution and well washed with distilled water; they were dried, when necessary, by successive washings with alcohol and ether; a current of air was finally sucked through them by a filter pump. The alcohol and ether were freed from water by lime and calcium chloride, respectively. They were distilled from a glass-stoppered flask because cork or rubber pollute the distillate. The delivery tube of the flask was inserted far into the condenser, and a light packing of Swedish filter paper discouraged convection currents. The products left no residue on glass, and could therefore be safely used for drying purposes.

An important material was the rubber lubricant, which came into contact with the pure amalgams and solutions during many operations of the research. Pure gum rubber was dissolved in its own weight of hard paraffin by rubbing the heated mixture with a pestle. Sufficient soft paraffin was then added to bring the lubricant to the proper consistency. The whole was then strained through a clean cotton cloth. It is difficult to imagine the presence of metals, decomposable sulphur compounds, or acids in the product.

[39] Zeit. Phys. Chem., 33, 611 (1900).

PRECAUTIONS USED IN THE PREPARATION OF AMALGAMS.

Zinc and cadmium amalgams in contact with air or aqueous solutions containing air are rapidly oxidized. As early as 1863 Crova complained of the inconstancy of the potential of amalgams "when the proportion of the oxidizable metal is extremely small;" he says that "continual agitation lessens the error but does not nullify it." St. Lindeck, in 1888, mentions the same difficulty. Meyer, in 1891, prepared potassium and sodium amalgams in an indifferent gas, and delivered them through fine jets into a solution free from air. Richards and Lewis weighed and kept their zinc and cadmium amalgams under solutions of the corresponding sulphate—a precaution which we found, from preliminary experiments, to retard oxidation, but not to prevent it altogether. Cady worked with amalgams of calcium and other oxidizable metals under pyridin. In a word, it appeared impossible to determine potentials within one hundred thousandth of a volt unless the exclusion of oxygen gas from every part of the process was complete. As will appear from the description of the experiments, the success of the following measurements was proportional to the completeness of this exclusion. Finally this cause of error seems to have been wholly overcome.

Clean, dry amalgams of known concentration were made from the pure materials as follows:

The best zinc sulphate was dissolved in pure water to form a saturated solution, which was then somewhat diluted. Ammonia was generated in a glass-stoppered distilling flask by heating a strong commercial solution of the gas, and passed into the zinc sulphate solution through a bent delivery tube; no cork or rubber was used in the apparatus. A heavy precipitate of zincic hydroxide redissolved at length to form a clear solution, but the current of ammonia was continued a little longer to avoid the formation of zincic hydroxide at the anode during electrolysis. The electrodes were of platinum foil about 1 sq. cm. in area. Platinum wires were welded to them. Before using they were boiled with strong nitric acid and washed with distilled water. The current density was large, but any tendency to form black or spongy deposits was carefully avoided.[40] Since zinc alloys somewhat with a platinum cathode, the layer next the platinum was not disturbed. The outer layer was removed from time to time to a beaker containing dilute distilled ammonia. When a sufficient quantity had been collected it was washed on a bare Gooch crucible with dilute distilled ammonia, distilled water, pure alcohol, and ether. The crystals were then exposed over night on a watch glass over strong sulphuric acid in a vacuum

[40] Proc. Am. Acad., 34, 89 (1898).

desiccator. In the morning suitable portions of the zinc and of pure mercury were weighed out into a small tube provided with a ground-glass stopper.

Since it proved difficult to combine dry zinc or cadmium with mercury without heating, it became desirable to shake them together under some reagent capable of dissolving the superficial film of oxide. The same procedure was adopted in diluting some of the amalgams with mercury. Dilute ammonia is suitable for the purpose, because it attacks pure zinc and cadmium but slightly and because the last traces of it are removed in a vacuum. The gas was distilled into pure water until the solution had acquired a strong odor. The reagent thus obtained was poured upon the components of the amalgam in the stoppered tube, and vigorous shaking continued until the process of solution was complete. The analysis of the aqueous solution for dissolved zinc and cadmium was carried out volumetrically with a solution of potassic ferrocyanide, 9.6 grams of the crystallized salt per liter, a dilute copper sulphate solution being used as an outside indicator. To standardize the ferrocyanide a weighed quantity of electrolytic zinc was dissolved in dilute sulphuric acid, made up in a graduated flask, and known volumes were titrated under the conditions later prevailing in the analysis of unknown solutions.

This same ferrocyanide solution produces a very insoluble precipitate in solutions of cadmium salts, but the composition is not $Cd_2Fe(CN)_6$, as one might expect.[41] The various formulas proposed by different authorities are all capable of generalization in the expression $Cd_xK_y[Fe(CN)_6]_{\frac{2x+y}{4}}$. Evidently we are dealing with a mixture or loose molecular compound of $Cd_2Fe(CN)_6$ and $CdK_2Fe(CN)_6$ in proportions that vary considerably according to concentration effects and temperature. Under the conditions of the work here described, the standard ferrocyanide solution was consistently found by a number of analyses to be equivalent to 0.00299 gram of zinc and 0.0029 gram of cadmium per milliliter.

A dilute solution of ammonia that has been shaken with pure mercury gives no precipitate with potassic ferrocyanide; therefore it is safe to assume that the zinc or cadmium content was determined by the volume of ferrocyanide added, minus one final drop, whose size was estimated from 0.01 to 0.04 cc. according to the volume of the ammonia solution and the intensity of the end-point noted. The estimation was based upon a series of blank experiments. For some very dilute solutions an excess of the ferrocyanide solution was added and the resulting opacity compared with a known suspension of a second precipitate. The latter was diluted until equal opacity was reached, and the familiar calculation made.

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[41] Journ. Am. Chem. Soc., 22, 537 (1900).

The amalgams made up by the method described above were separated from the supernatant liquid and bottled up clean and dry in suitable reservoirs with the help of the device shown in figure 2. *G* is a hydrogen generator of the Richards type, in which hydrochloric acid containing about 8 per cent of the anhydrous gas and the best obtainable grade of granulated zinc were used. A trace of cupric chloride was added to hasten the action. The gas thus obtained was purified by passing it through three Emmerling towers, E_1, E_2, and E_3, each 50 cm. high and 5 cm. in diameter, filled with glass pearls moistened with a very strong solution of pure caustic soda. The gas thus obtained contains no acids that might attack the amalgams, and is

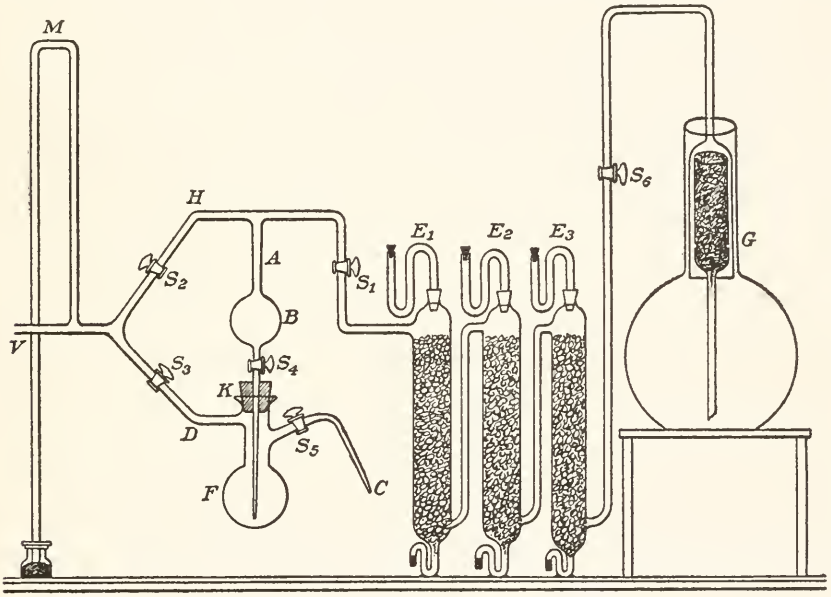


FIG. 2.—DEVICE FOR PRESERVING AMALGAMS.

fairly dry. The pipette *B* is fused at *A* to the delivery tube, and also communicates with the vacuum through *H* and *V*. The outlet tube of *B*, terminating in a thick-walled capillary, passes through the rubber stopper *K* into the flask *F*, which is provided with two sidenecks, *C* and *D*; *C* is fused to an open capillary, and *D* is connected with the aspirator. S_1, S_2, S_3, S_4, S_5, and S_6 are glass stopcocks well lubricated with paraffin-rubber lubricant. The only rubber in the apparatus proper, the stopper *K*, was boiled with sodic hydroxide solution and several portions of distilled water; before using it was covered with soft paraffin. The consistent use of fused joints prevents leakage and the introduction of sulphur compounds from rubber.

The apparatus thus arranged and scrupulously clean and dry is manipulated as follows: First, S_1, S_2, and S_5 are closed, and S_3, S_4, and S_6 left open; the pressure in B and F is reduced to 1 or 2 cm. of mercury, after which the rubber tube V is clamped off beyond M to test for leakage. If M remains at exactly its original height for one minute it is assumed that no leakage occurs. Then S_3 is closed, and S_1 cautiously opened, filling the system with hydrogen. This operation is performed three times, after which the air in the capillary C is expelled by a stream of hydrogen. Then S_5 and S_4 are closed, and S_3 opened, exhausting F once more; the tube C is then plunged below the surface of the amalgam under ammonia in the weighing tube, and S_5 cautiously opened. In this way all the amalgam can be sucked into the flask practically free from moisture. As the last of it passes S_5 the flow is stopped. Maintaining a low pressure in F, a rapid stream of hydrogen gas is bubbled through the amalgam to mix it and to eliminate the last traces of water and ammonia. After five or ten minues S_3 is closed, and F filled with hydrogen; S_1 and S_4 are closed and B evacuated through S_2. Then S_4 is cautiously opened, and the amalgam sucked into B, filling not more than 10 per cent of the entire volume. The vacuum is now shut off, and B filled with hydrogen communicating with the outside air through S_2. The tube A can now be sealed off from the generator without admission of air. Its end is bent into a hook to allow of suspension from a balance. Tube D is cut with a file, and B detached from F. The pipette is labeled and placed in a rack with its fellows (figure 3). The ammonia in C is added to the main portion in the weighing tube, and titrated as before described.

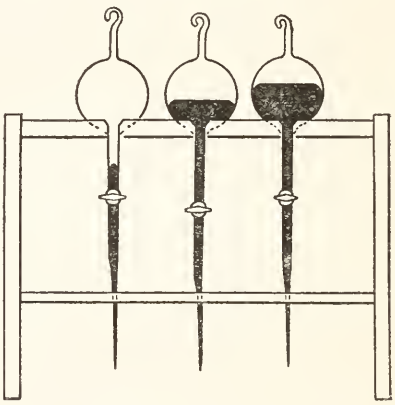


FIG. 3.—RACK WITH PIPETTES CONTAINING AMALGAMS.

Amalgams prepared in this way are perfectly clean and bright and remain so indefinitely. The weight of the column in the outlet tube permits the withdrawal of practically all the amalgam when the stopcock is opened. No access of air is possible except at the very small surface at the end of the capillary E, and even this small effect can be eliminated by running out a drop of amalgam before beginning a determination.

The solution of zinc or cadmium sulphate was freed from air in the apparatus just described. The liquid was introduced into the flask F like an

amalgam, then with S_3 open to the vacuum a rapid stream of rarefied hydrogen was passed through the solution for some time. It is believed that this process removed the remaining air. Finally S_3 was closed, and F allowed to fill with hydrogen, after which the solution was drawn up into B in the usual way. When the connection at A was fused off, the outlet of B was drawn out into a fragile capillary and sealed. Of course, when the solution was wanted, its weight was not sufficient to draw it out. To follow it up with hydrogen a well-cleaned rubber tube delivering hydrogen was forced over the fragile capillary; when this was broken communication with the gas generator was established.

Some previous investigators have allowed their electrolytes to stand over amalgams for some time before using it in the cells.[42] Zinc sulphate, fifth normal, was left in Jena glass over amalgam of the purest materials for several weeks before the first measurements, with occasional stirring. Perhaps the partial absorption of dissolved oxygen by the amalgam thus attained is helpful. However this may be, a pure sulphate solution freed from air by a stream of hydrogen can be used with perfect safety without putting it through this lengthy process.

THE CELL AND ITS MANIPULATION.

The cells used in the potential measurements must now be described. Figure 4 gives a good idea of the appearance of one of these just after a determination. The other cell used was different in one respect—its cups were all the same size. Very careful annealing of this apparatus is necessary. The advantages of this arrangement are marked. Four different amalgams can be introduced at one filling, and six direct potential measurements obtained under exactly the same conditions. Great economy of time and material are thus secured, and more important still, valuable checks on the accuracy of the measurements. These will be discussed later. The principle might, if necessary, be extended to cells containing even more cups.

The cell, clean and dry, was suitably supported in the thermostat, and the tube A fused to the outlet of a hydrogen generator similar to that shown in figure 2, and like it made of a single piece of glass. A double gridiron of glass tubing allowed considerable play without the introduction of a rubber connection, but the tubes B, C, D, E, were closed by clean rubber tubes and pieces of glass rod. The rubber surface exposed to the atmosphere of the cell was very small. The system as far back as the stopcock S_1 was evacuated through S_2 by a very efficient mechanical hand pump, and then filled with hydrogen through S_1. After this operation had been performed

[42] Richards and Lewis, Proc. Am. Acad., 34, 87 (1898).

three times, one of the glass rods was removed and the tip of the solution pipette inserted while hydrogen was issuing from the fine opening. The issuing stream of hydrogen prevented the diffusion of air into the cell. When the body of the cell was about half full, the solution pipette was withdrawn and the various amalgam pipettes successively inserted in the tubes *B, C, D, E*. Suitable portions of the amalgams were run in. Finally the platinum electrode wires, sealed into tapering glass tubes, were introduced, and the cell was ready for use.

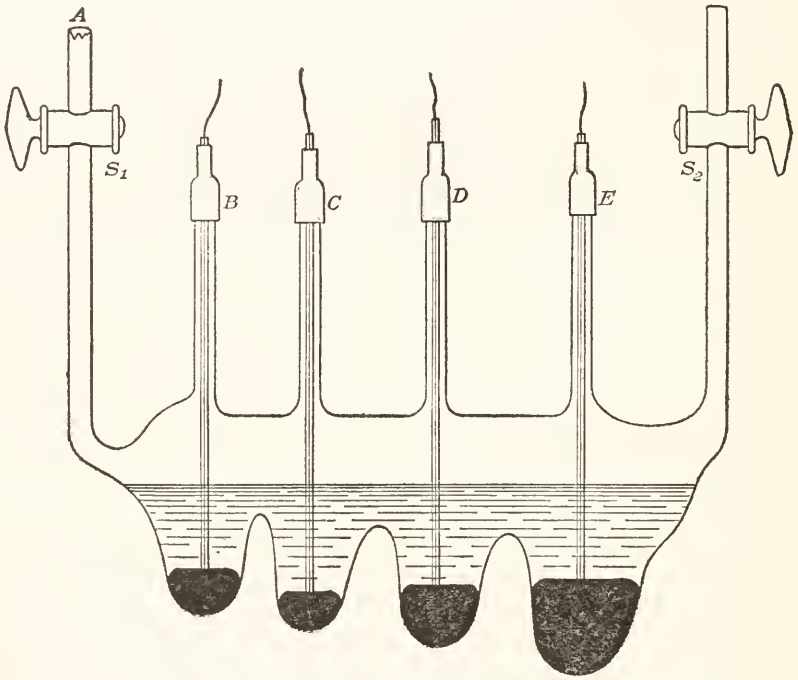


FIG. 4.—AMALGAMS IN CELL READY FOR POTENTIAL MEASUREMENT.

The temperature of the thermostat was kept constant within a hundredth of a degree by the familiar electrical regulating device shown in the diagram (figure 5). The mercury column, instead of cutting off a gas supply at *Q*, cuts off the current through the incandescent lamp hung in the water until the water cooled sufficiently to allow the circuit to be broken again at *Q*. An efficient centrifugal stirrer operated by a small electric motor kept the water in rapid circulation. The variation in temperature noted on a sensitive Beckmann thermometer graduated to one-hundredth never exceeded five one-thousandths of a degree. Although it was not important to know the temperature of the cell within nearer than 0.05° it was nevertheless

necessary that the different amalgams should be maintained at exactly identical temperatures; hence the care taken about this point.

The centigrade temperature was read from a thermometer graduated to tenths of a degree and permitting the estimation of hundredths, which was compared from time to time with a Reichsanstalt thermometer. The zero point of the latter was determined in ice and distilled water. Small corrections to the bore had been determined by comparison with a very accurate Baudin thermometer.

THE POTENTIOMETER AND ITS CALIBRATION.

The potentiometer shown in figure 5 was designed to give direct readings accurate to a few millionths of a volt. A fall of potential of 1 volt in the 10,000 ohms between *B* and *P* corresponds to 0.000001 volt for each 0.01 ohm; therefore, to attain the required degree of precision, all resistances to be included between the poles of unknown cells must be known within a few hundredths of an ohm. Since not more than one-twentieth of the entire fall of potential was ever neutralized in this manner, the other parts of the system need be standardized only one-twentieth as carefully. As a matter of fact the box *A*, containing nine 100-ohm coils and ten 10-ohm coils, was calibrated to 0.01 ohm, and the external resistances to 0.1 ohm. For the purpose a method of substitution, very similar to one recommended by Ostwald,[43] was adopted. In each comparison all four arms of the comparing bridge were of the same order of magnitude, so that the most sensitive and reliable adjustment was secured. All connections whose resistance could influence the results were made with great care. Extra heavy brass connectors were clamped upon the polished pegs of box *A* with the help of pliers; heavy copper wires were used as leads, and their ends were either soldered or amalgamated and dipped in the mercury cups of the rocker switch. The plugs used in comparing the bridge box were polished and driven home so well that the total resistance of the bars and connections measured only 0.006 ohm—a negligible amount. Heavy wires were used in the rocker switch, and all their joints were soldered.

The table of corrections was constructed as if the resistances had been weights,[44] the unit of reference being the value of the whole potentiometer box as 1,000 nominal ohms. The accuracy of the table was established in a wholly satisfactory manner by the direct comparison of several nominally equal combinations; in every case the observed results coincided with those predicted from the table.

[43] Ostwald-Luther, Hand- und Hülfsbuch, p. 355.

[44] Richards, Journ. Am. Chem. Soc., 22, 144 (1900).

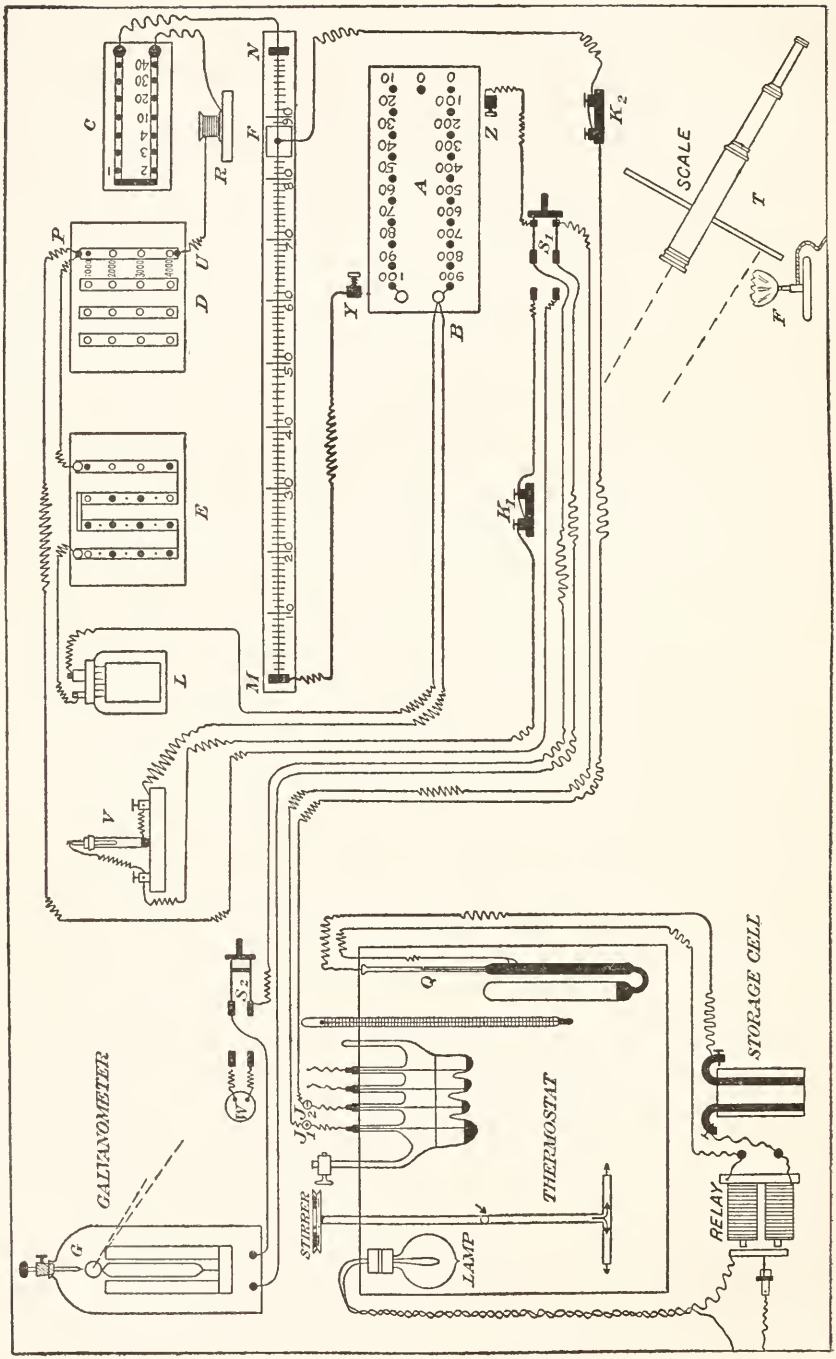


FIG. 5.—THE APPARATUS FOR MEASUREMENT OF POTENTIAL.

A troublesome problem was encountered in the division of the 10-ohm coils of box *A* into 100 parts to read to hundred thousandths of a volt. At first it was thought that the double shunt device suggested by Richards and Lewis [45] for the same purpose would be sufficient.

The shunts were both standardized and a complicated method of applying the corrections worked out. Needless to say, the labor of adjusting this device was severe; but unfortunately the results obtained with it were not wholly consistent. For instance, the cups of the cell were filled with various amalgams, which we will call *A, B, C,* and *D.* The potentials between *A* and *B, B* and *C,* and *C* and *D* were separately determined, corrected, and added up. Then the potential between *A* and *D,* derived in the same manner, was compared with this sum. The resulting values were respectively 0.05085, and 0.05081 nominal volt. Other similar experiments, hardly more satisfactory than the one just described, led us to abandon the method. Probably the fault lies in the excessive number of movable connections necessary in the apparatus, which answers well when less accuracy is demanded.

The final arrangement is shown in figure 5. *MN* is a manganin wire of nearly 10 ohms resistance and 90 cm. in length; its extremities are soldered to the upper surfaces of the brass plates at *M* and *N.* A long strip of glass fits accurately between these, and forms a satisfactory bed for the wire. The whole is mounted upon a well-seasoned slab of whitewood, bearing a scale which divides *MN* into 100 equal parts. A heavy copper wire is soldered at one end to *M,* and at the other to the heavy brass connector *Y,* which can be clamped firmly upon any 10-ohm peg in the box *A. N* was connected to a resistance box, *C,* which contained 10, 20, 30, and 40 ohm coils. The resistance from *P* to *U,* plus the small coil *R,* plus the slider, equals nine times the resistance of box *A.* If, however, the movable connector *Y* is moved from its present position in the course of a measurement, *n* times 10 ohms are cut out of the circuit. To maintain the rate of fall of potential at its original value, the proper resistance is introduced from *C.*

L was a Leclanché cell, whose potential was about 1.4 volts; its current ran through the parts of the system so far described, and also through a variable resistance, *E,* of about 4,200 ohms. By properly adjusting *E,* the potential between *B* and *P* could be made equal to that of the 1-volt cell *V* within 1 part in 14,000. The switch S_1 is thrown toward K_1, and when the 1-volt cell was just balanced by the fall of potential between *B* and *P,* no deflection of the galvanometer *G* was noted on closing the key K_1. The Helmholtz cell *V* was made with great care from pure materials, as recommended by Ostwald,[47]

[45] Proc. Am. Acad., 34, 91 (1898).

[47] Ostwald-Luther, Hand- und Hülfsbuch, p. 364.

and its potential was very constant, though not exactly equal to 1 volt. Its standardization will be considered on page 29.

The galvanometer G was a sensitive instrument of the d'Arsonval type. Its resistance was nearly 300 ohms. The glass front, which was imperfect, was removed, and the galvanometer was completely inclosed in a tight wooden box not shown in the diagram. A small window of optical glass was placed in the side of the box opposite the mirror, and the opposite wall was covered with black paper. The influence of drafts and of annoying reflections was thus avoided. Deflections were observed through a telescope, T, combined with a graduated scale; the portion of this, whose reflection was seen in the telescope, was illuminated by a small gas flame, F, placed at a safe distance from any junction of unlike metals. A thousand ohms could be introduced into the galvanometer circuit by means of the switch S_2 when circumstances required it. The whole apparatus was set up in a room of constant temperature.

The cell for containing the amalgams and the method followed in setting it up have already been described. The terminal wires, with great care to avoid momentary short circuits, were attached to brass binding posts, J_1 and J_2, mounted on an ebonite base clamped to the rim of the thermostat. The resistance in E was now adjusted as previously described, after which the switch S_1 was thrown over toward K_2. Then the potential of the unknown cell was neutralized within a millivolt by placing the connectors Y and Z on the proper pegs, y and z, of box A. After this approximate adjustment, the compensation of potential was completed by moving the platinum contact F along the slide wire MN until on pressing the key K_2 no deflection was noted in the galvanometer. Positive indications could be obtained from this instrument from changes in the position of the slider corresponding to five millionths of a volt. Therefore, no interpolation was necessary to get the fifth place correct to within half a unit. To make assurance doubly sure, a point five millionths of a volt on either side of the zero, giving swings of the galvanometer in opposite directions, was always noted.

The total value, x, of the slider was determined under the conditions actually prevailing in potential measurement. A certain cell was made to read very nearly 0.03200 nominal volt by suitably adjusting its temperature. The following readings were then obtained:

	Box A.	Corrected.
(1)	$\pi = 0.03300 + 0.025\,x$	$\pi = 0.032984 + 0.025\,x$
(2)	$\pi = 0.03200 + x$	$\pi = 0.03199 + x$

Therefore by subtraction we have $0.000994 = 0.975\,x$.

Hence the fall of potential from one end of the slider to the other is 0.00102 volt.

The scale of the slider was calibrated with the help of a small potentiometer box, carefully standardized, containing ten 2-ohm coils. The extremities of the slider were soldered to the terminals of this box by heavy copper wires; after equilibrium of temperature was assured, the poles of a battery were attached at these points. Then with the help of a sliding contact connected through a galvanometer to the various pegs on the box, nine points on the slide wire were found where no deflection was noted. These could be referred to the known resistances of the bridge, and their error determined. The determination was then repeated with the box reversed. Because the slight corrections thus found were regular, it was assumed, as seems permissible, that the variation of the wire between these points proceeded at a uniform rate. The two errors of the slider can now be combined and corrected for together.

Reading on slider.	Corrrection due to whole wire.	Correction due to error of scale.	Total correction in volts $\times 10^{-5}$
10	+0.2	+0.0	+0.2
20	+0.4	−0.2	+0.2
30	+0.6	−0.2	+0.4
40	+0.8	−0.3	+0.5
50	+1.0	−0.4	+0.6
60	+1.2	−0.3	+0.9
70	+1.4	−0.3	+1.1
80	+1.6	−0.3	+1.3
90	+1.8	−0.3	+1.5
100	+2.0	±0.0	+2.0

These values were used in the work on zinc. Eight months elapsed between the work on zinc and that on cadmium, and after that time the slide wire showed traces of corrosion. It was polished with very fine sandpaper and then restandardized with the same precautions as before.

Reading on slider.	Cadmium measurements. Correction in volts $\times 10^{-5}$.	Reading on slider.	Cadmium measurements. Correction in volts $\times 10^{-5}$.
10	+0.3	60	+1.4
20	+0.4	70	+1.5
30	+0.7	80	+1.8
40	+0.9	90	+2.2
50	+1.1	100	+2.6

The most serious sources of accidental error—partial short circuiting of points differing widely in potential, and thermoelectric currents—were constantly borne in mind. All switches and keys were mounted on glass, and all wires not carried in air lines were encased in glass tubes throughout their entire length. The apparatus was set up in a dry basement room which responded slowly to outside temperature changes. The absence of thermoelectric effects had to be inferred rather than proved. Brass, copper, and manganin, which have very small thermoelectric forces against each other,[48] formed most of the circuit, while platinum and German silver were sparingly used, and opposite junctions with other metals were always close together. Finally, the disposition of the apparatus seemed to offer no opportunity for large permanent temperature differences at various points.

Boxes *A* and *D* were of manganin; *A* was at least eight years old and *D* almost as well aged. Hence the relative values of the resistances can be assumed as constant over long periods.

THE STANDARD OF POTENTIAL.

All was now ready to measure the potential of concentration cells with an actual error not greater than five millionths of the 1-volt cell. Evidently the latter's value in absolute units must be known as accurately as possible. The standard at first relied upon was a large Clark cell of the usual form, bearing the stamp of the Reichsanstalt. As it had been in the laboratory for six years, it seemed wise to verify the statement of its potential as found in its certificate. Immediately after the close of the measurements on zinc, Professor B. O. Peirce, of the Department of Physics in Harvard University, examined it with great care, a service for which we are deeply indebted. His conclusions are quoted from his letter as follows:

> A hasty comparison made on Saturday of your normal Clark element with two standard cadmium cells, presumed to have the E. M. F. of 1.0186 volts at 21°, gave as the E. M. F. of the former 1.420+ at 21.5°. A more careful comparison made to-day gave 1.4206 with each cell at 21.5°, and since the element has been kept at practically a constant temperature for some time, the effect of time-lag may be assumed to have disappeared.
>
> I tested also five Carhart-Clark cells, and found that these differed considerably among themselves. As the E. M. F. of such a cell is likely to fall off, as times goes on, I chose that which had the highest E. M. F., and using Carhart's certificate of 1.4400 —0.00056 (t—15) as the E. M. F., got the same value as before (1.4206 international volts at 21.5°) for the E. M. F. of your element.

[48] Landolt und Börnstein (Meyerhoffer) Tabellen, p. 776 (1905).

In other words, the electromotive force of our standard has fallen off several tenths of 1 per cent from the value required by the Reichsanstalt formula for a Latimer-Clark cell at this temperature. Several days later, in reply to some inquiries concerning the variability of Clark cells of this type, Professor Peirce made a second very instructive investigation of this and other similar cells. He wrote as follows:

. . . I first tested against a certain cell used as a makeweight the four Muirhead standard cells, 10915l, 13361l, 10915r, 13361r, received a few months ago from the Cromptons to serve as standard units, with a very elaborate potentiometer made and tested by them. The readings were 1.4223, 1.4236, 1.4219, 1.4243, the cells being at 22.5° C. Your cell, which had been at 20.6° for some time, gave a reading of 1.4226 and a cadmium cell gave 1.0191. You will notice the comparatively large difference between the English cells, which are from a famous maker and have been tested by a well-known firm of electrical engineers. If 10915, as is probable, was made before 13361, the fall of E. M. F. with age seems to be indicated.

Of the Clark-Carhart cells A and B are seven or eight years old, I think; 264 and 265 are, I believe, more than six years old; 702, 706, 735, 737, and 740 are new (the oldest bears the date February 18, 1902, and carries a guarantee with proper treatment for three years, but I can not be sure that the laboratory has never fallen below allowable temperatures). The potentiometer readings were, at temperature in cells of 23.5°:

A	1.4257	265	1.3939	735	1.4335
B	1.4202	702	1.4337	737	1.4335
264	1.4260	706	1.4314	740	1.4325

The effect of age or wear and tear due to temperature changes and not to polarization in use seems clear.

Our cadmium cells are all almost exactly alike, and if for the sake of argument we assume that the E. M. F. of any one of them at room temperatures was 1.0185 true volts, and apply to them the slight temperature correction called for by the formula, the best two Muirhead cells would have E. M. F.s of about 1.4241 and 1.4248 at 21.5°, where the formula calls for 1.4248 true volts. The best three Carhart-Clark cells would have at 21.5° E. M. F.s of about 1.434 instead of 1.436, and your cell would have at 21.5°, the E. M. F. 1.4206, which was nearly what I got the other day.

Professor Peirce's exhaustive work establishes our potential standard beyond the possibility of doubt.

The formula used for the temperature coefficient $\pi_{t^\circ} = \pi_{15^\circ} - 0.0012(t - 15)$ is substantially the same as that given by the Reichsanstalt.

The comparison of the 1-volt cell with the standard Clark element was made on the standardized potentiometer already described, in the usual way.

After the reading, the 1-volt cell was returned to its original position to prove that the potential of the Leclanché cell had remained constant.

Professor Peirce's value for the Clark cell, corrected for its temperature coefficient, time-lag being eliminated as nearly as possible, established the potential of the 1-volt cell as follows:

Electromotive Force of Standard Helmholtz Cell.

No.	Time of observation.	T. of Clark cell.	X at t_0.
1	Before work on zinc.....	19.7°	0.9924 at 21°
2	After three measurements...	20.2	.9925 at 20
3	After seven measurements..	22.6	.9927 at 24
4	Near end of work	20.6	.9926 at 21
			π = 0.9925 at 21°

The average, $X = 0.9925 + 0.00007\ (t - 21°)$ international volts, is safe to use on all measurements of zinc concentration cells.

Eight months elapsed before the final determinations on cadmium concentration cells were made. Standardizations against the Clark cell now gave inconstant results, apparently due to the more rapid temperature changes of the laboratory during the winter. The average of four determinations indicated that $X = 0.9931$ volt at 19°. It seemed unlikely that the Helmholtz cell had changed as much as this; but on the other hand, the Clark cell was known to have fallen off considerably in six years, and may well have continued to do so since its standardization in June. Finally Mr. R. W. Kent, of this laboratory, kindly lent two cadmium cells, carefully made up from pure materials as recommended by Carhart and Hulett[49] and at least a week old. When opposed to the 1-volt cell, they each gave very nearly 0.0261 of X, which was measured on the potentiometer like the electromotive force of a concentration cell. Using the formula $\pi = 1.0186 + 0.00004\ (20 - t)$ international volts,[50] a potential $X = 0.9927$ was established for the 1-volt cell at 19°. This value is practically the same as that observed in June. It appeared more reliable than the slightly different verdict of the Clark cell, and was adopted for all measurements on cadmium concentration cells,

$$X = 0.9927 + .00007\ (t - 19°).$$

THE ELECTROMOTIVE FORCE BETWEEN ZINC AMALGAMS.

The work on zinc amalgams is conveniently considered first. Before presenting the quantitative data, a few more details must be reviewed.

All the zinc amalgams were made by successive dilutions of two liquid amalgams, No. 1 and No. 3, both of which were made from zinc and mercury. There was some question as to the accuracy with which the pure zinc described above could be weighed out; hence the true concentration ratio of No. 1 and No. 3 was not known with as much precision as could be attained in the dilution of each separated. Direct evidence could have been secured

[49] American Electrochemical Society Trans., 5, 59 (1904).

[50] Ostwald-Luther, Hand- und Hülfsbuch, p. 362.

by a potential measurement, calculating $\frac{c_1}{c_2}$ from the equation in which π and T were known. As this was not done, no amalgam derived from No. 3 was ever measured against any derived from No. 1. Two independent sets of results were thus secured, which by their agreement established certain conclusions beyond a reasonable doubt.

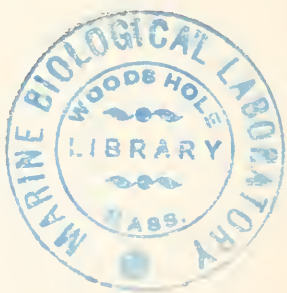
The possibility of polarizing the most dilute amalgams during measurements was considered. Momentary currents ranging from 0.001 to 0.00001 volt and flowing in alternate directions through a resistance of a thousand ohms can transfer only infinitesimal amounts of zinc. Still, the expected potential was roughly calculated before measurements, to avoid excessive differences at the first contact, and before the final readings were made the cell was shaken to renew the surface of the amalgams.

The data and calculations for a typical case follow:

Composition of Amalgam.

(1) Pipette of amalgam No. 3	=	121.543
(2) Pipette of amalgam No. 3	=	106.845
Amalgam No. 3	=	14.698
(1) Tube + mercury	=	112.26
(2) Tube + mercury	=	69.32
Weight of mercury	=	42.94
Weight of amalgam No. 3	=	14.70
Total weight of diluted amalgam	=	57.64

This diluted amalgam was called No. 4.



Zinc Dissolved in Ammonia during Mixing.

	Reading.
Ferrocyanide in burette (1)	46.25
Ferrocyanide in burette (2)	46.30
Ferrocyanide used	0.05
Needed for end-point	0.01
Total zinc dissolved	$0.04 \times 0.003 = 0.00012$ gram.

14.70 grams of amalgam containing 0.909 per cent of zinc, or 0.013 gram of zinc, were used; 0.00012 gram zinc is almost exactly 0.1 per cent of total. Therefore, the concentration ratio calculated from the weights of amalgam and mercury must be multiplied by 1.001 to correct for zinc dissolved.

The "parent" amalgam, 0.91 per cent, had density 13.465, at 20.00° C.

The new diluted amalgam, $\frac{14.7}{57.6} \times 0.91$ per cent, had density 13.527.

Then follows the calculation of the concentration ratio of the two amalgams, No. 3 and No. 4:

$$\frac{c_3}{c_4} = \frac{57.64}{14.698} \times \frac{13.465}{13.527} \times 1.001 = 3.908; \log \frac{c_3}{c_4} 0.59198.$$

In the same way the concentration ratios of other diluted amalgams made from No. 3 was calculated. These are recorded in the following table. The few necessary corrections for weights are included without comment, and the factors correcting for dissolved zinc are given without details.

Concentration Ratios of Zinc Amalgams. Preliminary Series (Cell I).

No. of amalgam.	Name of "parent" amalgam.	Weight of "parent" amalgam.	Weight of pure mercury.	Ratio of densities.	Factor correcting for dissolved zinc.	Approx. per cent zinc in amalgam.	$\log \frac{c_2}{c_n}$
3	Metallic zinc.[51]	1.116	120.98	.....	.....	*Per cent.* 0.909	0.00000
4	No. 3	14.698	42.94	$\frac{13.465}{13.527}$	1.001	0.232	0.59198
5	No. 3	7.114	105.96	$\frac{13.465}{13.540}$	1.0014	0.057	1.19951
6	No. 5	34.436	107.24	$\frac{13.540}{13.543}$	1.0015	0.014	1.81435

Having been thus prepared, the four amalgams, No. 3, No. 4, No. 5, and No. 6, were admitted into the four cups of the cell with all precautions, and the potentials were measured under the following conditions:

Temperature of thermostat (corrected) 23.09° C. = 296.17° abs.

Temperature of 1-volt cell = 21°; its potential was therefore 0.9925.

The formula for the calculation of π will be

$$\pi = \frac{8.316 \times T \times 2.3026}{2 \times 96580} \times \log \frac{c_1}{c_2}.$$

Log $\frac{c_4}{c_6}$ for the pair of amalgams No. 4 and No. 6 is found by subtracting

$$\log \frac{c_3}{c_4} \text{ from } \log \frac{c_3}{c_6}; \text{ because } \frac{c_3}{c_6} \div \frac{c_3}{c_4} = \frac{c_4}{c_6}.$$

[51] Of this zinc 0.006 gram was dissolved in ammonia during the amalgamation. Hence the weight of zinc dissolved in the mercury was 1.110 or 0.909 per cent.

Potentials of Zinc Amalgams. Preliminary Series (Cell I).

	Pair measured.	log $\frac{c_n}{c_m}$	π observed as a fraction of X.	π corrected for errors of potentiometer.	π in international volts.	π calculated for $t^\circ = 23.09^\circ C$.	Difference π calc. — π obs.
a	3–4	0.59198	0.016265	0.016267	0.016115	0.01738	+0.001265
b	4–5	0.60753	0.017685	0.017664	0.01753	0.017835	+0.000305
c	5–6	0.61484	0.018295	0.018267	0.01813	0.01805	−0.00008
d	3–5	1.19951	0.033885	0.033885	0.03363	0.03521	+0.00158
e	3–6	1.81435	0.05212	0.052123	0.06173	0.05326	+0.00153
f	4–6	1.22237	0.035915	0.035901	0.03563	0.03588	+0.00024

The sum of the first three potential differences must equal the fifth; otherwise a cyclic system furnishing work in violation of the laws of energy would be conceivable. As a matter of fact, their sum is 0.051775 instead of 0.05173, the sum of (a) and (b) is 0.033645 instead of 0.03363; the sum of (b) and (c) is 0.03566 instead of 0.03563. From an analysis of these figures it is clear that the values recorded in the first three cases are all too high; the error is more than 0.00001 volt in every instance.

Some constant defect, either in the potentiometer or in the method of using it, is indicated; but as this was the first time that formal measurements were made with the instrument, these errors may be excused if they do not occur again, and the results may be acceptable so far as they agree with the others. That both these conditions were satisfied will be evident on examination of the rest of the work.

The measurements of other similar cells were made with even greater care, and are recorded below:

Concentration Ratios of Zinc Amalgams. Second Series (Cell II).

No. of amalgam.	"Parent" amalgam.	Weight of "parent" amalgam.	Weight of pure mercury.	Ratio of densities.	Factor correcting for dissolved zinc.	log $\frac{c_2}{c_n}$
1	Zinc.	*1.1665	128.89	.....	.....	0.00375
2	No. 1	27.020	133.10	$\frac{13.467}{13.533}$	1.0025	0.77546
7	No. 1	21.530	22.667	$\frac{13.467}{13.509}$	1.0005	0.31504
8	No. 2	11.818	99.99	$\frac{13.533}{13.543}$	1.003	1.75236

*In amalgamating 0.005 gram of zinc was dissolved by ammonia; hence the amalgam contained 1.1615 grams of zinc, or 0.8932 per cent.

Potentials of Zinc Amalgams. Second Series (Cell II).

Temperature of thermostat (corrected) = 23.01° = 296.09° abs.
Temperature of 1-volt cell 20°; electromotive force = 0.9924.

	Pair measured.	log $\frac{c_n}{c_m}$	π observed as a fraction of X.	π corrected for errors of potentiometer.	π in international volts.	π calculated for t_0 = 23.01° C.	Difference π calc. − π obs.
a	1–7	0.31129	0.00838	0.008344	0.00828	0.009135	0.000855
b	1–2	0.77171	0.02140	0.021405	0.02124	0.02265	0.00141
c	1–8	1.74861	0.050165	0.050182	0.04980	0.05132	0.00152
d	7–2	0.46042	0.01306	0.01305	0.01295	0.013515	0.000565
e	7–8	1.43732	0.04182	0.041838	0.04152	0.042185	0.000665
f	2–8	0.97690	0.028805	0.028784	0.028565	0.02867	0.00105

Sum of (a) and (d) and (f) = 0.049795; (c) = 0.04980.
Sum of (a) and (f) = 0.02123; (b) = 0.02124.
Sum of (d) and (f) = 0.041515; (e) = 0.04152.

These agreements between sums of several potential differences, and the observed values of the totals are eminently satisfactory. In the rest of the final experiments, the checks obtained were uniformly as good as these; therefore, after this measurements made merely as a test of the accuracy of others will in general not be included in the tables of results.

The electromotive forces observed are constant throughout the day if the temperature of the cell remains unchanged. After forty-eight hours, during which time the supply of hydrogen had been discontinued and the thermostat had cooled down, cell II, when warmed up to its previous temperature, read as follows:

No.	New value observed.	Old value observed.
1–2	0.021415	0.02140
1–7	0.00839	0.00838
2–8	0.02888	0.028805
7–2	0.01307	0.01306

All the potential differences had increased, by an amount bearing a direct relationship to the dilution of the amalgam. The causes of the variation were probably the diffusion of oxygen from the air into the cell, or changes of concentration in various parts of the electrolyte due to evaporation and condensation on the upper part of the cell. The differences are not very great, however; and it is safe to conclude that the earlier values are correct.

Let us now attempt to generalize the results so far obtained: In all but one case the calculated potential exceeds the observed; the difference between the two, which from now on we will call $D\pi$, is the greatest when a

concentrated amalgam is compared with a weak amalgam, as in cell I *d*; and least when two weak amalgams are involved, as in cell II *f*; in one case of the latter kind, I *c*, the sign of the $D\pi$ has actually been reversed.

To exhibit the results graphically, the following plan might be adopted: Consider an imaginary series of cells, all having for one electrode a standard amalgam, A_3, containing 1 gram atom of zinc in the volume V_3, and for the other electrode different amalgams formed by diluting a given volume of A_3 to the new volumes $V_n, V_{n'}, V_{n''}$ . . . Plot the magnitudes of V as abscissæ and the potentials of the corresponding cells as ordinates; two curves, one for observed and the other for calculated potentials, result. The distance they intercept on any ordinate measures $D\pi$ for the cell which is defined by the position of that ordinate.

Plotted within a reasonable compass, these curves will not be sensitive enough to exhibit fully the accuracy of the work, since some of our potentials are known to 1 part in 5,000. If, however, the common logarithm of the concentration ratio is plotted as the abscissa and $D\pi$ as the ordinate, a very compact and sensitive curve can be drawn (figure 6).

Amalgam No. 3, the strongest used in the work, is taken as the standard, and all the others referred to it. As a matter of fact No. 3 was never actually compared with No. 1, but the calculated concentration difference was so slight that the point (1) can be interpolated without danger; its abscissa is 0.00375; and then its ordinate will be 0.00001. The measurements on amalgams derived from No. 1 start at that point as from an independent origin. In this way all the data so far obtained are made comparable.

The use of this curve is now easily extended to predict $D\pi$ for any cell containing two amalgams, A_m and A_n, of known concentration.

Let π_1 = potential calculated for cell $A_3 \rightarrow A_m$.
π_2 = potential calculated for cell $A_3 \rightarrow A_n$.
π_3 = potential calculated for cell $A_m \rightarrow A_n$.

Then

$\pi_1 - D\pi_1$ = potential observed for cell $A_3 \rightarrow A_m$.
$\pi_2 - D\pi_2$ = potential observed for cell $A_3 \rightarrow A_n$.
$\pi_3 - D\pi_3$ = potential observed for cell $A_m \rightarrow A_n$.

Now $\pi_1 + \pi_3 = \pi_2$ as proved before.

Also $(\pi_1 - D\pi_1) + (\pi_3 - D\pi_3) = (\pi_2 - D\pi_2)$ for the same reason.

Therefore, $D\pi_1 + D\pi_3 = D\pi_2$ and $D\pi_3 = D\pi_2 - D\pi_1$.

Hence it is unnecessary to calculate the values π_1 and π_2 at all; it is enough to find the logarithm of the concentration ratio of each amalgam in terms of A_3 correct to 0.01, to observe the two ordinates corresponding to these logarithms, and to subtract the smaller from the greater. The difference is $D\pi_3$, the desired quantity.

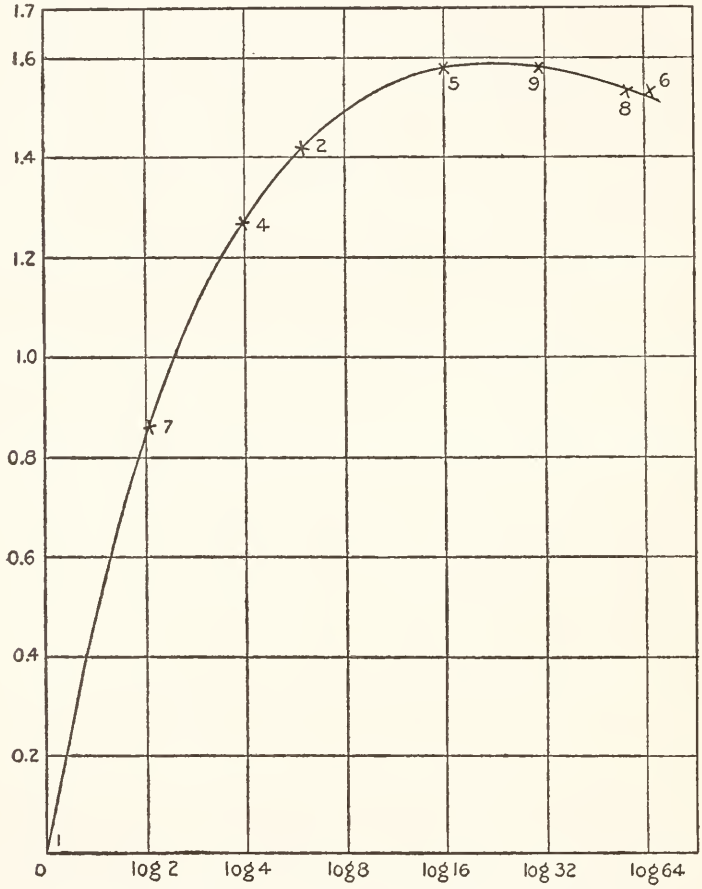


FIG. 6.—PRELIMINARY RESULTS WITH ZINC AMALGAMS.

Deviations from the theoretical potential are plotted in millivolts as ordinates; logarithms of the concentration-ratios as abscissæ. The most concentrated amalgam at the origin contained about 0.9 per cent of zinc. The downward curve at the right is due to oxidation.

Since $D\pi_1 + D\pi_3 = D\pi_2$ we can predict $D\pi_2$ if $D\pi_1$ and $D\pi_3$ are known. This method will be used again and again to get the total ordinate for amalgams which were not directly compared with A_3. Of course some risk of

cumulative error is involved, but the shape of the curve in its different portions—the most important question—can not be seriously altered, and the percentage error can never be increased.

It was now thought desirable to find a point on the curve between (5) and (8). Therefore, a new amalgam, No. 9, was made.

Weight amalgam No. 2	= 18.775
Weight mercury	= 77.90
Factor for Zn dissolved	= 1.002
Approximate per cent of Zn in No. 9	= 0.029

$$\frac{c_2}{c_9} = \frac{96.675}{18.775} \times \frac{13.533}{13.542} \times 1.002 + \log \frac{c_2}{c_9} = 0.71241$$

$$\log \frac{c_9}{c_2} = 0.77546$$

$$\log \frac{c_3}{c_9} \; 0.71241 + 0.77546 = 1.48787.$$

π (2-9) observed = 0.02088; corrected for errors in potentiometer, 0.02090; reduced to international volts 0.02074.

π (2-9) calculated = 0.020895; $D\pi$ for (2-9) = 0.000155.

Probable value for $D\pi$ (3-9) is the sum $D\pi$ (2-9) + $D\pi$ (1-2) and $D\pi$ (3-1).

$D\pi$ (3-9) = 0.000155 + 0.00141 + 0.00001 = 0.001575.

Point (9) fits the curve quite closely.

The curve as it now stands predicts that the potential between two amalgams containing less than four-hundredths of one per cent of zinc will be greater than that required by the osmotic formula; also that this effect will increase as infinite dilution is approached. The latter consideration points to experimental error rather than faulty assumptions in the formula, since infinite dilution usually minimizes disturbing secondary effects. Oxidation, the worst foe of workers in this field, was suspected; calculation showed that the absorption of 0.00003 gram of oxygen by each of the dilute amalgams, No. 4, No. 9, No. 6, and No. 8, would account for the falling off of the curve. It is quite possible that this quantity of the gas may have been absorbed on the glass surfaces used, or contained in the hydrogen bubbled through the amalgams, all our precautions notwithstanding. An amalgam so concentrated as No. 3 can not have been injured in this way; therefore, if weighed portions of it were diluted inside the cell with mercury free from air, the values of $D\pi$ thus determined would be free from error. Now, the risk of losing minute drops of amalgam from the pipette tips would make it inexpedient to weigh out less than 10 grams in each determination. It is inconvenient and wasteful to dilute such portions one hundred, fifty, or even ten times; there are also serious obstacles to the thorough mixing of such a com-

bination without a stirrer. Could it be possible to construct the last half of the true curve for $D\pi$ by convenient dilutions of the various weak amalgams inside the cell?

To solve this problem, imagine a series of cells where the concentration ratio is always equal to an arbitrary number—2, for instance. The first cell contains two concentrated amalgams, C_1 and C_2, while in succeeding cells the ratio is expressed in the general form $\frac{\frac{c_1}{m}}{\frac{c_2}{m}}$ where m is a number that can be increased at pleasure. At the beginning of the curve a comparatively small increment of m will produce a measurable change in the $D\pi$ of the cell. But far along on the curve, m may be varied considerably—several per cent perhaps—while $D\pi$ remains sensibly constant. Therefore, if this method of diluting amalgams is used, the true concentration of amalgam C_1 need not be certainly known within 1 or 2 per cent; the ratio alone is needed exactly when the dilution of the parent amalgam is already great.

Some preliminary trials of this method were now made. Pure mercury was drawn into a pipette similar to those used for amalgams, and sealed up without efforts to exclude air. The cell was set up and freed from air as usual, and a known portion of the very dilute amalgam No. 8 run in. The pipette was weighed before and after on a large balance reading at least to milligrams. The rapid succession of weighings made the use of a counterpoise unnecessary. Then a known weight of mercury was run into the same compartment of the cell. The pipettes were tapped before removal from the cell to dislodge loose drops from the capillaries. These were long enough to project into the body of the cell, but they did not touch the electrolyte. Under these circumstances the loss in weight of the pipette measures the quantity of substance introduced. Two dilutions by this method resulted in the amalgams No. 10 and No. 11, for which the concentration ratio was computed and the electrical measurements made. The densities of No. 8 and No. 10 are practically identical. There is no titration correction, of course.

Quantitative Data.

NO. 10.

Weight of amalgam No. 8,	18.740
Weight of mercury,	17.442
	36.182

$$\frac{c_8}{c_{10}} = \frac{36.182}{18.740}; \log \frac{c_8}{c_{10}} = 0.28573.$$

NO. 11.

Weight of amalgam No. 8, 9.845
Weight of mercury, 11.407
21.252

$$\frac{c_8}{c_{11}} = \frac{21.252}{9.845}; \log \frac{c_8}{c_{11}} = 0.33418.$$

Potential of Zinc Amalgams. Preliminary Trial of Dilute Solution.

π of 1-volt cell, 0.9928; t of thermostat = 23.08° C.

Pair observed.	π observed fraction of 1-volt cell.	π corrected fraction of 1-volt cell.	π in international volts.	π calculated.	$D\pi$.
8–10	0.00846	0.008425	0.00836	0.008325	0.000025
8–11	0.00983	0.00980	0.009725	0.009805	0.00008

These results seem to prove that $D\pi$ should be a positive quantity, even when both the amalgams introduced are extremely dilute. Since, however, $\log \frac{c_8}{c_{10}}$ is very nearly equal to $\log \frac{c_8}{c_{11}}$, the marked difference in values for $D\pi$ indicates experimental error; more care must be exercised in this process.

The only imaginable sources of error seemed to be loss of material in transferring, and failure to mix the mercury and amalgam thoroughly.

The first difficulty was obviated by the use of a capillary half a millimeter in diameter and somewhat tapered at its very end. The shaking of the cell was a tedious process, since the glass gridiron establishing a connection with the hydrogen generator allowed but little play. After fifteen seconds the observed potential was always equal, within a few units in the fifth place, to the limit approached on long-continued agitation. This limit was recorded as the true reading for the cell.

As might have been expected, the first reading was too high whenever the mercury was run in on top of the amalgam, and too low in the reverse case.

A new amalgam, No. 12, very nearly equal in concentration to No. 5, was now prepared. From it No. 13, No. 14, No. 17, and No. 18 were made by dilution in the cell as described above. Various peculiarities in the results were noted, but could not at first be explained. Finally oxidation was detected inside pipette No. 12, and careful examination revealed a very small hole, where the upper tube had been sealed off. Experiment showed that two different portions of this amalgam gave a considerable potential against each other. The remainder of No. 12 was thrown away, and all results obtained by its use rejected.

We now resolved to conduct a series of final measurements, repeating all those where amalgams more dilute than No. 2 were concerned, with extreme precautions against error. To exclude the last trace of air from the process, the purest mercury was redistilled directly into a pipette as follows: The condenser tube of the all-glass apparatus previously described was fused to the inlet of the pipette, as it lay in a horizontal position. The capillary tip was cut off below the stopcock, and in its place was fused the tube leading to the vacuum pump. The distillation was conducted as usual in a stream of hydrogen until 300 grams of mercury had collected in the hemisphere below the inlet and outlet tubes. Then the stopcock was closed, and the system filled with hydrogen. The inlet tube was now fused off into a hook as usual. No important amount of oxygen could have been present in the mercury or its atmosphere. The vacuum connection was now cut off and the capillary tip fused on in its place. The next problem was to replace all the air in the outlet tube with mercury. It will not suffice to hold the pipette upright and open the stopcock, since the mercury will run down into the capillary without filling the intervening section of larger tubing. The elasticity of the confined body of gas will allow mercury to spirt out at every jar, and will make accurate weighing impossible. Therefore, a one-hole rubber stopper receiving the outlet tube of the pipette was fitted into a heavy test-tube side-necked for a vacuum connection and a hydrogen supply. When all the air present had been replaced by hydrogen the pressure was slightly diminished and the tip of the pipette raised somewhat above the bulb; a column of mercury still clung in the tube connecting the stopcock to the bulb, and on opening the stopcock the mercury slowly rose into the outlet tube and filled it completely. On detaching the test-tube and stopper the pipette containing pure mercury free from oxygen was ready for use. With this pure mercury was accomplished the dilution of amalgams No. 2, No. 22, and No. 9 inside the cell, as follows:

The Dilution of Amalgam No. 2.—Quantitative Data.

	NO. 19.		
Weight amalgam No. 2	7.732	Ratio of densities	$\frac{13.533}{13.541}$
Weight mercury	13.985		
	21.717		

$$\frac{c_2}{c_{19}} = \frac{21.717}{7.732} \times \frac{13.533}{13.541}; \log \frac{c_2}{c_{19}} = 0.44825.$$

NO. 20.

Weight amalgam No. 2 8.631
Weight mercury 19.017
28.248

Ratio of densities $\frac{13.533}{13.542}$

$$\frac{c_2}{c_{20}} = \frac{28.248}{8.631} \times \frac{13.533}{13.542}; \log \frac{c_2}{c_{20}} = 0.51467.$$

NO. 21.

Weight amalgam No. 2 6.690
Weight mercury 12.236
18.926

Ratio of densities $\frac{13.533}{13.542}$

$$\frac{c_2}{c_{21}} = \frac{18.026}{6.690} \times \frac{13.533}{13.542}; \log \frac{c_2}{c_{21}} = 0.45133.$$

Potentials of Zinc Amalgams. Fourth Series; Dilute Amalgams.

π of 1-volt cell = 0.9926; t of thermostat = 23.10° C.

Pair observed.	π observed fraction of 1-volt cell.	π corrected fraction of 1-volt cell.	π in international volts.	π calculated.	Difference $D\pi$ —
2–19	0.013085	0.013076	0.1298—	0.01316	0.00018+
2–20	0.01505	0.015027	0.01491	0.01511	0.00020
2–21	0.01317	0.013161	0.01306	0.01325	0.00019

Here might have been inserted the check measurements with standard amalgam, which were just the same.

The next portion of the curve to be investigated lay beyond the point (5). Amalgam No. 5 was so nearly used up that a new amalgam, No. 22, had to be prepared and bottled in the original apparatus.

Weight amalgam No. 1 10.50
Weight mercury 157.54
166.04

Correction factor for *Zn* 1.0016
Ratio of densities $\frac{13.464}{13.540}$

Its concentration in terms of No. 1,

$$\frac{c_1}{c_{22}} = \frac{168.04}{10.495} \times \frac{13.466}{13.542} \times 1.0015; \log \frac{c_1}{c_{22}} = 1.20262.$$

Concentration referred to No. 3 $\log \frac{c_3}{c_{22}} = 1.20637.$

π (1-22) observed	0.03402
π (1-22) corrected	0.033996
π (1-22) international volts	0.03374
π 1-22 (calculated)	0.03530
$D\pi$	= 0.00156
Total ordinate, 0.00156 + 0.00001	= 0.00157

When 3-5 was measured $D\pi$ was 0.00158 for almost exactly a corresponding dilution. This indicates that the oxidation effect in the bottling process is very nearly constant.

Returning to the question of dilution of amalgam 22 inside the cell, we have:

Quantitative Data.

NO. 23.

Weight amalgam No. 22	12.606
Weight mercury	13.463
	26.069

Ratio of densities $\frac{13.542}{13.544}$

$$\frac{c_{22}}{c_{23}} = \frac{26.069}{12.606} \times \frac{13.542}{13.544}; \log \frac{c_{22}}{c_{23}} = 0.31547.$$

NO. 24.

Weight amalgam No. 22	11.473
Weight mercury	12.259
	23.732

Ratio of densities $\frac{13.542}{13.544}$

$$\frac{c_{22}}{c_{24}} = \frac{23.732}{11.473} \times \frac{13.542}{13.544}; \log \frac{c_{22}}{c_{24}} = 0.31559.$$

Potentials of Zinc Amalgams. Fifth Series; Very Dilute Amalgams.

π of 1-volt cell = 0.9925; t = 23.09° C.

Pair observed.	π observed fraction of 1-volt cell.	π corrected fraction of 1-volt cell.	π in international volts.	π calculated.	Difference $D\pi$.
22–23	0.009325	0.009285	0.009215	0.00926	0.000045
22–24	0.00933	0.00929	0.00922	0.009265	0.000045

This was one of the most pleasing measurements in the research; before the potentials were calculated, the accidental agreement of these two observations occasioned surprise. When the calculations were finished, it was seen that the predicted values also were very close together; the slight difference between them was of the expected size and in the proper direction.

The Dilution of Amalgam No. 9 Inside the Cell.—Quantitative Data.

NO. 15.

Weight amalgam No. 9	12.424
Weight mercury	14.835
	27.261

Ratio of densities $\frac{13.543}{13.544}$

$$\frac{c_9}{c_{15}} = \frac{27.261}{12.424} \times \frac{13.543}{13.544}; \log \frac{c_9}{c_{15}} = 0.34125.$$

NO. 16.

Weight amalgam No. 9 13.101
Weight mercury 15.846
28.997

Ratio of densities $\frac{13.543}{13.544}$

$$\frac{c_9}{c_{16}} = \frac{28.947}{13.101} \times \frac{13.543}{13.544}; \log \frac{c_9}{c_{16}} = 0.34427.$$

Potentials of Zinc Amalgams.—Final Series; Very Dilute Amalgams.

π of 1-volt cell = 0.9925; t = 23.09° C.

Pair observed.	π observed fraction of 1-volt cell.	π corrected fraction of 1-volt cell.	π in international volts.	π calculated.	Difference.
9–15	0.01005	0.01006	0.00998	0.010015	0.000035
9–16	0.01013	0.01014	0.01006	0.01010	0.00004

These results, of great consistency and trustworthiness, make possible the construction of the true curve for $D\pi$ beyond point 2. For this purpose it is convenient to start at point 2, which may be assumed for the moment as correctly placed; its abscissa is 0.077546, and its ordinate, referred to No. 3 by interpolation, is 0.00141 + 0.00001 or 0.00142.

Amalgam.	Total abscissa $\frac{c_3}{c_n}$	Total ordinate $D\pi_n + D\pi_m$
19	0.77546 + 0.44825 = 1.22371	0.00142 + 0.00018+ = 0.00160+
20	0.77546 + 0.51467 = 1.29013	0.00142 + 0.00020 = 0.00162
21	0.77540 + 0.45133 = 1.22679	0.00142 + 0.00019 = 0.00161

The curve is now extended from point 2 through points 19, 20, and 21; the ordinate (log $\frac{c_3}{c}$ = 1.20637), representing nearly enough the true concentration of amalgam No. 22 intersects it at the point 22; the value of the ordinate is thus fixed as 0.00160. Starting again from this point, the curve may be extended to amalgams 23 and 24.

Amalgam.	Total abscissa $\frac{c_3}{c_n}$	Total ordinate $D\pi_n + D\pi_m$
23	1.20627 + 0.31547 = 1.52184	0.00160 + 0.000045 = 0.001645
24	1.20637 + 0.31559 = 1.52196	0.00160 + 0.000045 = 0.001645

In like manner the value of the ordinate ($\log \frac{c_3}{c_9} = 1.48787$) is fixed as 0.00164, and the curve extended to the still greater dilution of amalgams 15 and 16, made from amalgam 9.

Amalgam.	Total abscissa $\frac{c_9}{c_n}$	Total ordinate $D\pi_n + D\pi_m$
15	1.48787 + 0.34125 = 1.82912	0.00164 + 0.000035 = 0.001675
16	1.48787 + 0.34427 = 1.83214	0.00164 + 0.00004 = 0.00168

On plotting these values (figure 7), the improvement due to the rigid exclusion of oxidation is manifest.

The close approach of the "oxidation curve" to the true curve in the region of point 2 shows that amalgam No. 2 was not measurably affected by oxidation; this effect became manifest only with very dilute amalgams; it was obviously due to the oxygen absorbed during some part of the complicated manipulation involved in the earlier experiments.

Lack of time prevented the investigation of the extremely dilute amalgams beyond points 15 and 16. It seems safe to conclude, however, that the observed potentials will continue to approach their calculated values still more closely as the dilution is increased, for the curve is evidently becoming more and more nearly horizontal as the dilution proceeds—that is to say, is approaching more and more nearly to the requirements of the gas law. It is to be noted that even amalgams 15 and 16 are very dilute, containing only about 0.014 per cent of zinc by weight. This matter will be discussed further when the results with cadmium have been given.

In concluding this portion of the work, it is worth while to point out that the success of the measurements depended wholly upon the chemical side of the investigation, namely, upon the purification of the materials, and especially upon the rigorous exclusion of oxidation. The physical measurements of course demanded great care, but they involved nothing new. On the other hand, the effect of the few hundredths of a milligram of oxygen would have wholly vitiated the results if this oxygen had not been wholly excluded; and the detection and elimination of this cause of error caused the chief labor of the research and determines its value.

INFLUENCE OF THE CONCENTRATION OF THE ELECTROLYTE.

The electrolyte used in the original measurement of Nos. 1-22 was analyzed by titration with ferrocyanide solution. Its concentration was very nearly one-tenth molal. A new electrolyte was made up from chemically pure zinc sulphate, ten times as strong as the above, and this was freed

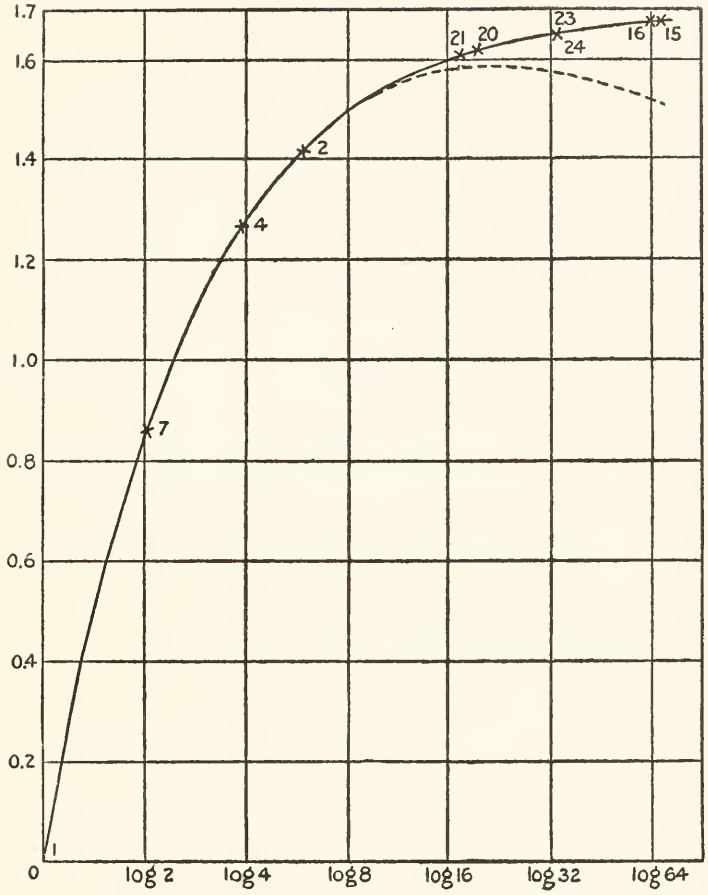


FIG. 7.—FINAL RESULTS WITH ZINC AMALGAMS.

Deviations from the theoretical potential are plotted in millivolts as ordinates, logarithms of the concentration-ratios as abscissæ. The most concentrated amalgam at the origin contained about 0.9 per cent of zinc. The dotted curve is a repetition of figure 6; the continuous curve represents the better results not vitiated by oxidation.

from air as before. With this new electrolyte measurements of the cell 1-22 were repeated, with the result $\pi = 0.03401$, instead of 0.03402 as before. These values are practically identical; hence the conclusion of Richards and Lewis [52] that the potential of these cells is independent of the concentration of the electrolyte is confirmed. There is every reason, from a theoretical point of view, for the acceptance of this conclusion.

[52] Proc. Am. Acad., 34, 93 (1898).

THE POTENTIAL BETWEEN CADMIUM AMALGAMS.

The study of cadmium was now taken up, in the same general manner as that just described. Four amalgams were made from the first sample of pure electrolyzed cadmium, and bottled up in pipettes exactly as in the case of zinc.

The very dilute amalgams, 5, 6, 7, and 8 were made inside the cells by dilution with distilled mercury in hydrogen.

Concentration Ratios of Cadmium Amalgams.

No. of amalgam.	"Parent" amalgam.	Weight of "parent" amalgam.	Weight of pure mercury.	Ratio of densities.	Factor correcting for dissolved Cd.	$\log_{10}\frac{c_m}{c_n}$
1	Cadmium.	[53] 4.530	148.88	.....	.....	.....
2	No. 1.	24.17	74.08	$\frac{13.372}{13.593}$	1.0007	0.60509
3	No. 1.	8.949	125.79	$\frac{13.372}{13.534}$	1.0025	1.17359
4	No. 3.	35.29	94.13	$\frac{13.534}{13.542}$	1.001	1.73812
9	Cadmium.	1.361	44.525	.....	.....	.....
5	No. 1.	12.226	12.762	$\frac{13.371}{13.458}$	1.000	0.30759
6	No. 2.	12.113	11.599	$\frac{13.503}{13.523}$	1.000	0.89616
7	No. 3.	15.205	15.246	$\frac{13.534}{13.540}$	1.000	1.47501
8	No. 3.	20.526	59.818	$\frac{13.534}{13.542}$	1.000	1.76599

From these amalgams two quadruple cells were made up, and their electromotive forces measured with all possible care.

The first cell contained amalgams 1 and 2 as well as 5 and 6. Its temperature was 23.03°. The potential of the 1-volt cell was 0.9926 volt.

The sum of (1-6), (5-2), and (2-6) is 0.026875; the direct measurement of (1-6) gives 0.02687; other similar checks are equally satisfactory; hence the potentiometer readings are still reliable.

[53] This value is corrected for the small amount of cadmium dissolved by ammonia during amalgamation. The amalgam contained 2.9553 per cent of cadmium.

Potentials of Cadmium Amalgams. First Series.

Pair measured.	π observed as a fraction of X.	π corrected fraction of X.	π in international volts.	$\log_{10} \frac{c_m}{c_n}$	π calculated for t_0.	Difference π calc.— π obs.
1–5	0.009505	0.009472	0.009405	0.30759	0.00903	—0.000375
1–2	0.018428	0.018405	0.01827	0.60509	0.01776	—0.00051
1–6	0.027098	0.027067	0.02687	0.89616	0.02630	—0.00057
2–6	0.008690	0.008664	0.00860	0.20107	0.00854	—0.00006
5–2	0.008052	0.008935	0.00887	0.29750	0.00873	—0.00014
5–6	0.017615	0.017597	0.01747	0.58857	0.01727	—0.00020

The second cell contained amalgams No. 2, No. 3; also No. 7 and No. 8, made by the dilution of No. 3 inside the cell to about one-half and one-quarter its original concentration.

Its temperature was 23.03° C. = 296.11°, and the potential of the Helmholtz cell was $X = 0.9929$.

Potentials of Cadmium Amalgams. Second Series.

Pair observed.	π observed as a fraction.	π corrected fraction of X.	π in international volts.	$\log_{10} \frac{c_m}{c_n}$	π calculated for t_0.	Difference π calc.— π obs.
3–8	0.017580	0.017562	0.017437	0.59240	0.017387	—0.00005
3–7	0.008955	0.008935	0.008873	0.30142	0.008846	—0.00003
2–3	0.016915	0.016906	0.016785	0.56850	0.016685	—0.00010
7–8	0.008657	0.008631	0.008570	0.29098	0.008540	—0.00003

Calculated from 3-8 and 3-7, the value of $D\pi$ for 7-8 is — 0.00002, while from the direct reading the value is —0.00003.

No matter how satisfactory a set of readings appears, it should be checked by a determination in duplicate. A fresh portion of cadmium was therefore made by electrolysis and converted into amalgam No. 9, designed to have as nearly as possible the same concentration as No. 1.

Weight of cadmium	1.361
Weight of mercury	44.527
Cadmium dissolved in ammonia	0.0084
Percentage content of Cd No. 9, calculated	2.949
Percentage content of Cd No. 1, calculated	2.953
Density of amalgam .9 =	13.471

From No. 9 two amalgams were made by dilution inside the cell as usual.

NO. 10.

Weight amalgam No. 9 11.730
Weight mercury 18.077
29.807

Ratio of densities $\frac{13.372}{13.478}$

$$\frac{c_9}{c_{10}} = \frac{29.807}{11.730} \times \frac{13.372}{13.478}; \log \frac{c_9}{c_{10}} = 0.40159.$$

NO. 11.

Weight amalgam No. 9 11.516
Weight mercury 64.08
75.596

Ratio of densities $\frac{13.372}{13.520}$

$$\frac{c_9}{c_{11}} = \frac{75.596}{11.516} \times \frac{13.372}{13.520}; \log \frac{c_9}{c_{11}} = 0.81242.$$

Potentials of Cadmium Amalgams. Third Series.

$t = 23.00°$ $X = 0.9928$

Pair observed.	π observed as a fraction of X.	π as a corrected fraction of X.	π in international volts.	$\log \frac{c_m}{c_n}$	π calculated for t_c	Difference π calc. — π obs.
9–10	0.01230	0.012302	0.012215	0.40159	0.011785	—0.00043
9–11	0.24585	0.024578	0.02440	0.81242	0.023845	—0.000555
9–1	0.00002	0.00002	0.00002	0.00088	.....	.....

The curve for $D\pi$ in cadmium amalgam cells can now be constructed on the same principles employed in the case of zinc. The two starting points are so nearly identical that no interpolation is necessary. The summary follows.

Deviations of Cadmium Amalgam Cells.

Amalgam No.	Total abscissa $\frac{c_1}{c_n}$	Total ordinate $D\pi_n + D\pi_m$
1	0.00000	± 0.00000
2	0.60509	— 0.00051
3	1.17359	— 0.00061
[54] 4	1.73812	— 0.000675
5	0.30759	— 0.000375
6	0.60509 + 0.29107 = 0.89616	— 0.00057
7	1.17359 + 0.30142 = 1.47501	—0.00061—0.00003 = — 0.00064
8	1.17359 + 0.59240 = 1.76599	—0.00061—0.00005 = — 0.00066
9	— 0.00088	± 0.00000
10	0.40159	— 0.00043
11	0.81242	— 0.000555

[54] Interpolated from measurements at 30.00° and at 15.20° by use of absolute temperature measurements.

All these points lie upon a very satisfactory curve except point 4. It will be remembered that this amalgam was prepared outside the cell, as were Nos. 1, 2, and 3. The result shows that clearly amalgam 4 was dilute enough to begin to show the effect of oxidation, like that found in the case of zinc. On the other hand, oxidation has evidently not caused an appreciable error in the ordinate 3; hence points (7) and (8), based upon point (3), are right also. The curve is plotted in figure 8.

Attention is called to the fact that this curve of potentials is very similar in form to that of zinc, except that the sign of its curvature is exactly opposite. This point will be discussed later.

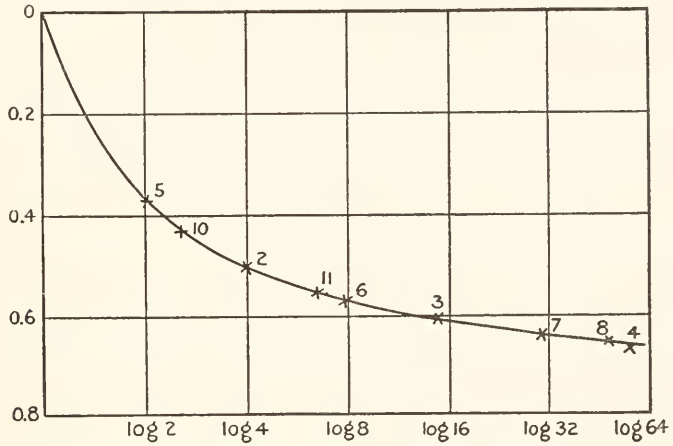


FIG. 8.—RESULTS WITH CADMIUM AMALGAMS.

Deviations from the theoretical potential are plotted as ordinates; logarithms of the concentration-ratios as abscissæ. The most concentrated amalgams at the origin contained 2.95 per cent of cadmium.

THE TEMPERATURE COEFFICIENT OF AMALGAM CELLS.

Three pairs of cadmium amalgams were investigated with great care at 30°, at 15°, and 0°. The warm thermostat (described above) maintained its temperature within one-hundredth of a degree. The intermediate bath had a cold-water coil more than sufficient to compensate for the warming effect of the surroundings; the adjustment of temperature was accomplished by an incandescent lamp with the usual electric cut-off. The lowest temperature was attained in a large zinc trough surrounded by cotton wool and placed inside a wooden box; clear ice, finely divided and nearly covered with distilled water, was used to maintain the temperature constant at 0° C.

All temperatures were read upon the Reichsanstalt thermometer already described; corrections were made for the zero point in melting ice, for the

known error of the scale, and for the exposed thread. Ample time was allowed for the cell to reach the temperature of the bath. The measurements follow:

Temperature Coefficient of Cadmium Amalgam Cells.

Pair observed.		π observed as fraction of 1-volt cell at 30.00°.	π in international volts at 30.00°.	π observed as fraction of 1-volt cell at 15.20°.	π in international volts at 15.20°.	π observed as fraction of 1-volt cell at 0.00°.	π in international volts at 0.00°.
I	2–4	0.034465	0.034204	0.032775	0.032545	0.031050	0.030826
	1–4	0.053291	0.052910	0.050668	0.050332	.....	.....
	1–3	0.036193	0.035900	0.034393	0.034130	.....	.....
II	2–4	0.03447	0.034209	.....	.....	.....	.....
	1–4	0.053295	0.052914	.....	.....	.....	.....
	1–3	0.036189	0.035896	.....	.....	.....	.....

The multiple cell after measurement at zero was returned to the warm thermostat, and fifteen minutes later it gave almost exactly its original readings (see series II). The results at 0° for combinations 1-3 and 1-4 are not given in the table, because at that temperature they showed an abnormally low potential, evidently due to a partial freezing of amalgam I; this is consistent with the observations of Korp and Böttger.[55] This fact does not, of course, interfere with their use at a higher temperature.

It becomes now a matter of great interest to compare this change of potential with the requirements of the gas law, by comparing the temperature coefficient with the temperature-pressure coefficient of a perfect gas over the same range of temperature.

The following table gives the temperature coefficients referred to the observed potentials at zero:

2-4, from 30.00° to 15.20°.

$$\frac{\Delta\pi}{\pi_0 \Delta t} = \frac{0.001659}{14.80 \times 0.030826} = 0.00364$$

2-4, from 15.20° to 0.00°.

$$\frac{\Delta\pi}{\pi_0 \Delta t} = \frac{0.001719}{15.20 \times 0.030826} = 0.00367$$

1-4, from 30° to 15.20°.

$$\frac{\Delta\pi}{\pi_0 \Delta t} = \frac{0.002578 \times 288.20}{14.80 \times 273.08 \times 0.050332} = 0.003655$$

1-3, from 30° to 15.20°.

$$\frac{\Delta\pi}{\pi_0 \Delta t} = \frac{0.00177 \times 288.20}{14.80 \times 273.08 \times 0.034130} = 0.00366$$

Average 0.00366 +

[55] Zeit. Anorg. Chem., 25, 59 (1900).

The agreement is surprisingly good; within the limit of accuracy of the measurement the increase of the potential with increase of temperature is identical with the increase of pressure of a perfect gas. A strong presumption in favor of the constancy of $\frac{d\pi}{dT}$ at all temperatures is established by these measurements.

Time did not permit a careful study of the temperature coefficient of pairs of zinc amalgams, but enough was done to show that the agreement was almost as good in this case also. This matter will be discussed presently from another point of view.

THE MEASUREMENT OF THE HEAT OF DILUTION OF THE AMALGAMS.

The next important step in the experimental work was to determine directly the heat of dilution, in order to apply rigorously not only the equation of Helmholtz,

$$\nu\pi F - U = \nu F \frac{d\pi}{dT}$$

but also the equation of Cady and of Lewis,

$$\nu\pi F - U = \nu F \, ln \, \frac{V_2}{V_1}$$

and thus to throw light on the cause of the deviations noted in the curves discussed in the previous sections.

The great consistency and accuracy of the preceding electrical measurements makes it highly desirable that the heat of dilution, which in this case is the heat of reaction of the system under investigation, should be determined with great precision. In order to show the grade of accuracy needed, attention is called to the fact that each hundred thousandth of a volt in the potential of a concentration cell corresponds to the development of two joules during the transport of a gram atom. Consider now a gram atom of zinc contained in 7 kg. of amalgam 3 in the act of dilution with an equal volume of mercury. The heat capacity of the reacting mixture will not be far from 2,000 mayers;[56] hence two joules will produce in it a temperature change of one-thousandth of a degree. If the thermometer can be read as accurately as this, the accuracy reached in the work on potentials will be maintained. The same dilution of a gram atom of cadmium in cadmium amalgam No. 1 will involve a heat capacity only about half as great; here, therefore, the thermometer will be read twice as accurately as the potentiometer. If the amalgam resulting from either of the above reactions is diluted with its own

[56] A mayer is the heat capacity raised 1° C. by a joule.

volume of mercury, the heat developed by the reaction is distributed over a heat capacity double that noted above. Then the thermometer must be read twice as accurately as before estimated, in order to compensate for this fact.

Extending this train of reasoning, it is evident that excessive refinement in temperature measurement would be required to obtain a good experimental value for the heat of reaction of more dilute amalgams, where the heat capacity per gram molecule of zinc is enormous. Limitations in time made it necessary to confine our attention to concentrated amalgams. In all probability the generalizations established for these cases will apply at greater dilutions also.

The measurement of the heats of dilution presents considerable experimental difficulties. Practical considerations make it desirable to limit the weight of mercury used in one experiment to 5 kg.; but the small heat capacity of such a mass and its rapid conduction of heat demand extraordinary constancy in the temperature of the surroundings. Owing to the high inertia of mercury and its low heat capacity, efficient stirring of the mixture is likely to produce a marked rise in temperature; this must be estimated and the corresponding correction applied. Moreover, the entire process must be carried out in an indifferent gas, to prevent oxidation, with its attending development of heat.

To meet these requirements a new form of calorimeter was devised. The principle of the divided vessel was suggested by the work of Richards and Lamb,[57] but it is believed that other features of the apparatus constitute a new departure in the study of small heats of reaction.

The calorimeter *C* is shown in figure 9. It was made of flexible thin iron plate seamed together. The partition *P* slid in deep grooves, *b* and b^1, while its lower edge was received by a shallow trough of sheet iron cemented to the bottom of the calorimeter; when *P* is in this position its top is flush with the rim of the vessel. A grease containing about one part of gum rubber, five of hard paraffin, and ten of soft paraffin applied around the edge of the partition made either side of the vessel mercury-tight. When the ebonite support *R* had been attached, *C* was lowered into the copper cylinder *F*, leaving an air space 0.7 cm. in thickness.

A weighed amount of pure mercury was now run into one side of *C* from a separating funnel. Then the clockwork stirring apparatus was lowered into *F* and bolted rigidly to brass ledges soldered to the inner wall of *F*. The mechanism consisted merely of the spring, its arbor, and one gear, whose shaft carried the paddle *D*. The latter now dipped into the mercury, but its blades lay flat against the partition *P*; therefore, when the spring was wound up the paddle could not revolve until *P* was pulled out.

[57] Richards and Lamb, Proc. Am. Acad., **40**, 657 (1905).

The ebonite cover to the copper cylinder F, pierced with suitable holes, was now screwed to brass ledges soldered to the inner wall of the cylinder, 2 cm. below its rim. The cracks were stuffed with tissue paper. F was then lowered into an empty thermostat, of capacity about 80 liters, and a tube delivering a rapid stream of pure dry carbon dioxide was fitted into its proper hole in the cover. The outlet for the tube gas was exactly in the

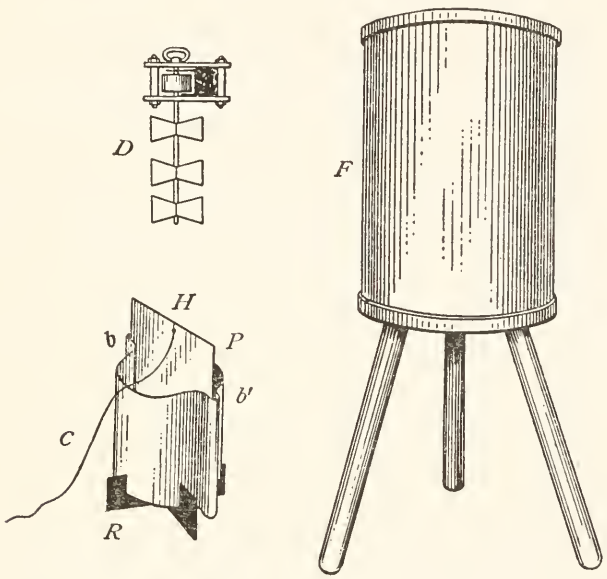


FIG. 9.—PORTIONS OF THE APPARATUS FOR MEASURING THE HEAT OF DILUTION.

center of the cover and contained a wire attached to the partition at H; the wire passed through a small greased rubber tube fitted with a pinchcock, while the gas escaped through a sideneck. When all air was displaced, a weighed amount of the amalgam to be diluted was run into the empty half of C from a separating funnel filled with carbon dioxide. A Beckmann thermometer was then lowered into the hole, and clamped firmly in place, its bulb half way between the surface and the bottom of the amalgam. All the tubes leading into the calorimeter were also clamped, after which the tenth of a liter of a mixture of hard and soft paraffin melting at about 45° Centigrade were poured upon the ebonite cover. This, when hard, made the vessel F water-tight; but as an additional precaution a small outward pressure of carbon dioxide was always maintained by closing all outlets. The thermostat was now filled well above the top of F, and regulated by a very large and sensitive electric cut-off. The make and break was in an arti-

ficial atmosphere of hydrogen, and responded to a change of one or two thousandths of a degree. Needless to say, a powerful stirrer was used to keep the bath in rapid circulation.

The thermostat was allowed to run all night before a determination; in the morning the Beckmann thermometer was absolutely stationary at the temperature of the bath outside. The partition *P* was pulled out by means of the wire mentioned above; the paddle, when thus released, revolved about fifty times before the spring ran down. The temperature change was read off on the Beckmann thermometer with careful tapping to avoid friction of the thread.

Unless mercury and amalgam are in perfect thermal equilibrium before the experiment, the initial temperature, read from the single thermometer in the amalgam, will not represent the average temperature of the reacting mixture. Seventeen hours at constant temperature on all sides should insure this condition for a comparatively small volume of a substance conducting heat so well as mercury. Blank runs, however, were made with pure mercury to test the truth of the assumption thus made. No cooling correction, of course, was necessary, though five minutes were allowed for the thermometer to become constant.

Blank experiment 1: Temperature change + 0.001°.

Blank experiment 2: Temperature change + 0.006°.

This irregularity was found to be due to uneven heating of the calorimeter, by radiation from the lamp used for heating the thermostat. This radiant heat maintained one-half the mercury at a slightly higher temperature than the other, on a cold night when the lamp was in operation most of the time. On this account an electric heating coil 30 cm. in diameter was substituted for the lamp; its plane was horizontal, and the vessel *F* was exactly in its center. Uneven heating could not now occur, and the following blank experiments proved the change to have accomplished its object:

Blank experiment 3: The thermometer fell 0.001°, and then rose to its original position.

Blank experiment 4: The thermometer rose 0.002°.

The mean of these trials indicates that a correction of —0.001° in each experiment should suffice for our purpose. This is to be ascribed to the work done by the clockwork stirrer.

A zinc amalgam (0.9 per cent) was now made from pure stick zinc and mercury purified with mercurous nitrate. The manipulation of the two determinations of the heat of dilution of this amalgam has already been described.

Cooling Effect on Diluting Zinc Amalgam.

	Weight of mercury.	Weight of amalgam.	Temperature change.
	Grams.	*Grams.*	
I	2523	2303	−0.021
II	2303	2303	−0.0225

In the first case the stirrer probably ceased to revolve after a few revolutions; in the second case it worked efficiently. The mean fall of temperature in this cooling effect is 0.022°; corrected for the heat of stirring it becomes 0.023°.

The total energy change of dilution is equal to the product of the heat capacity and the temperature increment, 0.023°. The heat capacity is found as follows:

	Heat capacity, in mayers.
2,300 grams of mercury	317
2,300 grams of amalgam	[58] 320
130 grams of iron	60
5 grams of grease and cement (estimated)	16
Thermometer (estimated)	13
Total heat capacity	720

Therefore the energy-change was $720 \times -0.023 = -16.6$ joules.

The 2,300 grams of amalgam contained $\frac{2300 \times 0.0091}{65.4}$ mols of zinc.

Hence the total energy-change involved in the same dilution of a gram-atom of zinc is:

$$-16.6 \times \frac{65.4}{2300 \times 0.0091} = -52 \text{ joules.}$$

The further dilution of a zinc amalgam containing less than 1 per cent of zinc thus causes a very appreciable cooling effect.

The cadmium used to make amalgams for the investigation of heats of dilution was the commercial "pure" article, but of course its purity was not above suspicion. Inasmuch as the dilution of the small amount of impurity which it might contain could not cause an appreciable heat effect, its use was justifiable for these measurements. Even 2 per cent of zinc could cause at the most a temperature change of only 0.001°.

[58] This value was found in a special series of determinations to be described elsewhere.

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Absolutely no change of temperature was noted upon withdrawing the partition in either of two apparently perfect experiments on the dilution of this 3 per cent cadmium amalgam. If the clockwork stirrer caused heat enough to raise the temperature 0.001°, the dilution of the cadmium amalgam could not have had a cooling effect on dilution of much more than this. Therefore, it seems probable that the total internal energy-change involved in the dilution of a 3 per cent cadmium amalgam by pure mercury is negligibly small, not over 1.0 joule per gram atom; and it is further probable that the dilution of cadmium amalgams of lower concentrations absorb even less heat.

Before accepting these results, a determination on pure mercury and on each amalgam was made by another method. The clockwork was dispensed with, and a second thermometer inserted so that one thermometer was immersed in each of the liquids to be mixed. A hand stirrer whose shaft was incased in a long glass tube projected into the calorimeter. The other features of the process remained unchanged. After a long time at constant temperature the partition was pulled out and hand stirring begun. As expected, the vertical motion of a small circle of glass rod was far less satisfactory than the automatic paddle which it replaced; the rate of mixing, as inferred from the movements of the thermometers, was slow, and the clumsy stirring was attended by the evolution of much heat. The superposition of this effect upon the true heat of dilution gave rise to ill-defined results. None of these, however, threw doubt on the measurements obtained by the first method; hence the extremely small heat effect in the dilution of cadmium amalgams was confirmed.

It may here be stated that besides these calorimetric experiments, others were instituted in order to determine the change of heat capacity of a metallic system during amalgamation.[59] The heat capacity of both zinc and cadmium amalgams were studied, and were found to be slightly, but only slightly, greater than some of the heat capacities of the mercury and other metal before mixing. The difference was so slight that it is safe to assume that the further dilution of either amalgam involves no appreciable change of heat capacity. Hence these experiments need not be described in detail here; they will be recounted at length in another place.

[59] Richards, Henderson and Forbes, Proc. Am. Acad., **41**, 8 (1905).

THE APPLICATION OF THE EQUATION OF HELMHOLTZ.

According to the equation of Helmholtz,[60]

$$\pi\nu F - U = \nu F T \frac{\Delta\pi}{\Delta T}$$

the sum of the heat of reaction and the product of the absolute temperature and the temperature-coefficient of the change of free energy should equal the change of free energy itself.

In the case of the cadmium cell it is possible to prove the rigorous application of this equation, because all the quantities are known.

For example, taking the cell 2-4 (which gives about the average temperature coefficient), we have

$$\begin{aligned} \pi_0 &= 0.030826 \text{ volt} \\ \Delta\pi &= 0.001719 \text{ volt} \\ \Delta T &= 15.20^\circ \\ T &= 273.09^\circ \\ \nu &= 2 \\ F &= 96{,}580 \\ U &= -0.001 \end{aligned}$$

Therefore, for the left-hand number we have

$$5.95 - 0.001 = 5.95 \text{ kilojoules}$$

and for the right-hand $= 5.95$ kilojoules

showing a difference of .00

The difference between the two members of the equation is thus certainly less than the probable magnitude of the experimental error. No more satisfactory verification of this equation has ever been offered; and the case is of especial interest because of the extremely small value of the heat of reaction.

The Helmholtz equation can not be supported in the same way by the results with zinc, because lack of time prevented us from determining its temperature-coefficient with sufficient accuracy. On the other hand, knowing the heat of dilution on doubling the volume of a 0.91 per cent zinc amalgam to be — 0.052 kilojoules (see page 55), the temperature-coefficient of a cell of this kind can easily be calculated with the help of the Helmholtz equation. Transposed for this purpose[61] the equation becomes

$$\frac{\Delta\pi}{\Delta T} = \frac{\pi}{T} + \frac{52}{2 \times 96{,}580 \times T}$$

[60] In this case $\Delta\pi$ and ΔT can be substituted for the infinitesimals, as the heat capacity does not change on dilution.

[61] See Richards and Lewis, Proc. Am. Acad., 34, 88 (1898).

Selecting the cell 1-7 (see page 34) as representing the dilution in question, we have the following data: $\pi = 0.00828$, $T = 273.09° + 23.01° = 296.1°$; therefore, $\frac{\pi}{T} = 0.00002796$ and $\frac{52}{2 \times 96{,}580 \times T} = 0.00000099$. Hence $\frac{\Delta\pi}{\Delta T} = 0.00002892$. From this it is easily calculated that π at 0° is 0.00762 and $\frac{\Delta\pi}{\pi_0 \Delta T}$ is 0.00379. It is interesting to note that through a partial compensation of opposite effects this temperature-coefficient of electromotive force should be brought to within about 3 per cent of the temperature-coefficient of pressure-increase in a perfect gas (0.00366). Previous experiments[62] were not accurate enough to detect any difference at all between these values. The present values are more trustworthy, because the most doubtful quantity, the last term above $\left(\frac{52}{2 \times 96{,}580 \times T}\right)$ can hardly be in error by an amount which would affect the result 0.3 per cent.

THE APPLICATION OF THE FORMULA OF CADY.

While there is thus every reason to believe that the Helmholtz equation applies with great exactness to the phenomena under consideration, the case is very different with equation of Cady,

$$\nu\pi F = RT \ln \frac{v_2}{v_1} + U, \text{ or } \pi - \frac{RT}{\nu F} \ln \frac{v_2}{v_1} = \frac{U}{\nu F}$$

This equation is now to be considered.

Selecting again similar cells for this comparison, we have for the cadmium cell 1-5 from the table on p. 47.

$$\pi - \frac{RT}{\nu F} \ln \frac{v_2}{v_2} = + 0.000375 \text{ volt}$$

and from p. 56 $$\frac{U}{\nu F} = \frac{1.0}{2 \times 96{,}580} = - 0.000005 \text{ volt}$$

$$\text{Difference} = + 0.00038 \text{ volt}$$

This difference corresponds to about forty times the probable error of the potential readings, and nearly eighty times the probable error in the estimation of the heat of dilution; moreover, the quantities are actually different in sign.

The deviation in the case of zinc is even more marked, although in this case the two members of the Cady equation at least have the same sign. The figure for the potential of a cell made from amalgam 3 and one only half as concentrated are less by 0.00085 than the theoretical value based on

[62] Richards and Lewis, Proc. Am. Acad., 34, 94 (1898).

the volumes, and the heat of dilution was found to be —52 joules for an amalgam equally concentrated. Hence

$$\pi - \frac{RT}{\nu F} ln \frac{v_2}{v_1} = - 0.00085 \text{ volt}$$

$$\frac{U}{\nu F} = - 0.00027 \text{ volt}$$

$$\text{Difference} \quad - 0.00058 \text{ volt}$$

This value has even a larger percentage accuracy than the one computed for cadmium, and like that one can not but signify a real discrepancy.

Because in neither case, then, the equation of Cady was found to hold exactly true, it is clear that some modifying influence must be at work. It does not by any means follow that the effects depicted by Cady's equation do not really represent part of the influences producing electromotive force; but clearly this equation does not contain a complete or exact account of all these influences.

THE PROBABLE CAUSES OF THE DEVIATIONS.

It becomes now a matter of great interest to speculate concerning the probable cause of the discrepancy; for an uncomprehended irregularity is always suggestive of unknown but possibly knowable effects.

Many possible superposed effects have been suggested as capable of modifying results of this kind. Of these the most important may be discussed in general before proceeding to particulars.

In the first place, it has been suggested that the space occupied by the dissolved substance should be taken into consideration. This was first suggested, perhaps, by A. A. Noyes,[63] when working with Ostwald, and has received striking support in the recent osmotic experiments of H. N. Morse already cited. The further suggestion of Noyes, that the volume of the molecules of *solvent* also should be subtracted, is of a more hypothetical nature, and seems to receive less support from the facts.

Secondly, the suggestion of compounds of solvent and solute (hydrates in aqueous solution, or hydrargyrates in mercurial solutions) has been made to explain many phenomena of the two classes of solutions. Marignac, de Coppet, and Rüdorff all considered this possibility and inclined toward it long ago. More recently H. C. Jones has revived the theory; and Haber's recent extension of it to mercurial solutions has already been discussed. There is nothing unreasonable in this idea.

Thirdly, it is conceivable that although the amalgam holds most of its dissolved metal in a monatomic form, a part remains polymerized, or in a

[63] Noyes, Zeitschr. Phys. Chem., 5, 53 (1890).

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hydrargyrate containing two or more atoms of the solute to the molecule. This equally plausible contingency simply postulates that a balanced reaction such as $2Zn \lesseqgtr Zn_2$ or $2ZnHg_n \lesseqgtr Zn_2Hg_{n-m} + Hg_m$ exists in the solution. Such a reaction would of course be pushed from right to left by diluting the amalgam.

It has been suggested also that changes of heat capacity should be considered in probing to the uttermost the equation of Cady. In the present case, however, this possibly disturbing effect is eliminated, for we have shown that the change of heat capacity which takes place on diluting either zinc or cadmium amalgam is so slight as to cause no suspicion that this phenomenon can have anything to do with the observed irregularities.

The most probable disturbing agencies having thus been discussed in general, the particular cases under consideration may be considered. As has been made clear, the amalgams of the two metals vary in opposite ways from the theory, cells of zinc amalgams giving potentials too low and cells of cadmium amalgam giving potentials too high. The two must, then, be considered separately; and of the two, cadmium may most conveniently be considered first, because it presents the least irregularity.

One of the striking facts in relation to cadmium amalgam is the fact that its heat of dilution is so small as to be negligible. Therefore, the equation of Helmholtz reduces practically to the form

$$\pi v F = v F T \frac{d\pi}{dT}$$

making the thermodynamics of the problem as simple as possible.

The only irregularity which this cell of cadmium amalgams manifests is the following, namely, with all except the most dilute amalgams

$$\pi v F > RT ln \frac{v_2}{v_1}$$

Thus from the volume-energy point of view the cadmium acts like hydrogen—a gas "more than perfect."

But in this equation the left-hand member represents a statement of fact, and R and T are definite quantities whose product is only very slightly uncertain. Therefore, it seems probable that the only remaining term, the ratio of v_2 to v_1, is not correctly chosen.

It will be remembered that this term was always evaluated on the assumption (1) that the metal dissolved in mercury is strictly monatomic, (2) that it forms no compound with the solvent, and (3) that it obeys the laws of perfect gases with exactness. If the first condition is not satisfied, the potential will be lowered; if the second or the third is violated, the reverse effect will probably prevail.

In the case of cadmium the observed potential is higher than the calculated value; hence either the second or third (or both) disturbing effects may be supposed to predominate over the first. It will be seen that these excessive values of the potentials with great concentrations are precisely parallel with the excessive values of osmotic pressures in concentrated aqueous solutions, observed especially by H. N. Morse and his assistants, in his very important researches on this subject. Here as there, the simplest explanation seems to be that a portion of the total volume is not effective as a receptacle for the dissolved cadmium; and it becomes highly interesting to speculate as to the magnitude of this useless space.

Any calculation of this kind must involve assumptions of some kind, and it is important that the assumptions should be as reasonable as possible. In a preliminary trial, it may be assumed that the useless space does not vary with the volume, and that there is complete absence of polymerization.

The ratio of the values of the useful space in the two amalgams may be derived at once from the following equation:

$$ln \frac{v_4}{v_3} = \frac{\nu\pi F}{RT} = W \tag{1}$$

when v_4 and v_3 are the ideal or hypothetical volumes of the useful space.

The actual ratio of the volumes is, however,

$$\frac{v_2}{v_1} = \frac{W_2 D_1}{W_1 D_2} \tag{2}$$

found directly from the weight W_1 and W_2 and the densities D_1 and D_2 of the two masses of amalgam containing the same weight of cadmium.

Now, calling the useless space b and assuming it to possess a constant value (that is, assuming $v_2 = v_4 + b$ and $v_1 = v_3 + b$) we have from (1)

$$ln \frac{v_2 - b}{v_1 - b} = \frac{\nu\pi F}{RT} \tag{3}$$

or from (2) and (3)

$$ln \left(\frac{\frac{W_2 D_1}{W_1 D_2} v_1 - b}{v_1 - b} \right) = \frac{\nu\pi F}{RT} \tag{4}$$

or,

$$b\left(1 - \text{anti } ln \frac{\nu\pi F}{RT} \right) = v_1 \left(\frac{W_2 D_1}{W_1 D_2} - \text{anti } ln \frac{\nu\pi F}{RT} \right).$$

Hence

$$b = v_1 \frac{\left(\frac{W_2 D_1}{W_1 D_2} - \text{anti } ln \frac{\nu\pi F}{RT} \right)}{\left(1 - \text{anti } ln \frac{\nu\pi F}{RT} \right)}. \tag{5}$$

Calculated thus, b in cell 1-5 is found to be 15.8 milliliters, in cell 1-2, 14.4 milliliters, in cell 2-5, 12.7 milliliters, and in cell 3-8, 21 milliliters, for an amount of amalgam containing a gram-atom of cadmium. Owing to the extreme dilution, the value for cell 3-8 has a very great probable error and may be rejected. The average of the others is 14.3 milliliters, a quantity very near the gram-atomic volume of cadmium, 13.0. Thus if from the actual volume of the amalgam the space originally occupied by the cadmium is subtracted, the remaining volumes v_5 and v_6 very nearly fulfill the equation

$$RTln \frac{v_6}{v_5} = \pi v F.$$

The following table illustrates this relation, and is comprehensible without further comment:

Designation of cell.	Potential of cell calculated from actual volumes.	Potential calculated from volumes after subtraction of volume of Cd.	Observed potentials.
1–5	0.00903	0.00933	0.00940
1–2	0.01776	0.01821	0.01827
2–5	0.00873	0.00888	0.00887

Evidently, while the correction greatly improves the agreement between the theoretical and the observed values, there is still a slight discrepancy, especially with the stronger amalgams. The "useless volume" is in most cases slightly larger than the volume of the cadmium. Does this signify that the cadmium expands on amalgamation, while causing the mercury which surrounds it to contract somewhat more than it expands? This is conceivable, although the total effect on amalgamating a gram-atom of cadmium is a contraction of about 1.3 milliliters, as calculated from the densities. Or, on the other hand, does some of the mercury, combining with the cadmium, remove itself from the possibility of functioning as a solvent and thus add to the useless volume? Yet another possibility also exists. It may be, as has been already suggested, that this value of the useless volume is really nothing but an accidental balance between the opposing tendencies—that the true value is really considerably larger, including at least a gram-atom of mercury in addition to one of cadmium, but that the true value does not appear because of the counterbalancing presence of polymerization. It will be seen that in the case of zinc this latter effect seems to be the predominant one.

Further light could be obtained by determining the osmotic pressure of the cadmium in solution, because this would be dependent upon the sum of the osmotic pressures of the various molecular species, instead of having their effect counterbalance. If the deviation of this value of the osmotic pressure

from the theoretical coincided with the inference from deviation in the electromotive force, it would be reasonable to suppose that both deviations were due to the same ultimate cause, and that this was the only cause.

The only results which seem to have been obtained upon this matter are those of Ramsay on the decrease of vapor pressure of mercury at 260° caused by the solution of a metal. He found the atomic weight of cadmium in three solutions containing 0.04, 1.08, and 1.92 per cent of cadmium to be 100.2, 99.7, and 103.8, respectively. Neglecting the first of these results, because the amalgam was then too dilute for sufficient percentage accuracy, the others give an average atomic weight of 101.8 (instead of the true value 112.5) for cadmium in an amalgam containing 1.5 per cent of this metal. The osmotic pressure was therefore about 10 per cent too great in this 1.8 atomic-normal solution. Such an excess is four times as large as that which would be caused by a "useless space" equal to the volume of the dissolved cadmium, for this amalgam is essentially like amalgam 5 of this paper, which has just been calculated to show a "useless" space of only about 2.5 per cent of the total volume.

In short, while both Ramsay's results and ours vary from the simplest theory in the same direction, they differ greatly in the amount of variation; and if both are to be trusted, taken together they point not only to the formation of hydrargyrates in the amalgam, but also to polymerization. Ramsay's results, nevertheless, need confirmation before they can be accepted without question, as they are not very numerous, and vary considerably among themselves. Further treatment of the matter must be postponed until more knowledge has been obtained concerning these osmotic pressures. The subject is being studied further in this laboratory.

The case of zinc may be reviewed more briefly, although it also presents very interesting features. Here, instead of giving too high an electromotive force, the zinc amalgams give one less than the theoretical. A part of this deficiency is to be ascribed to the thermal effect depicted by the formula of Cady; but as is shown on page 59 this formula explains only one-third of the total deviation. In view of the outcome of the preceding discussion, it seems necessary to refer the otherwise unexplained deficiency to the polymerization of a part of the zinc.

This assumption of polymerization is supported by all the other facts bearing upon the question. In the first place, we have found that the dilution of a 1 per cent amalgam absorbs considerable heat, showing that the same reaction which occurs on amalgamating is still occurring—and the cooling part of this reaction must be supposed to consist in the disintegration of the zinc. However, this effect must not be too hastily connected with the

splitting up of chemical union among the atoms; it might also be referred to a less definite attraction, one similar to that causing the Joule-Thomson effect in gases. In mercurial solutions this attraction would be the difference between two affinities, but for our purposes it can be treated as a single quantity. Now, in the free expansion of carbonic acid from ten atmospheres to normal pressure, a cooling effect of 1.4° C. occurs; if the molecular heat is taken as 40 mayers, 56 joules are absorbed by each gram molecule. When a gram-atom of zinc, in the calorimeter, expands from 44 to 20 atmospheres osmotic pressure, without doing outside work, 52 joules are absorbed. Clearly it would be possible to account for the cooling effect alone without assuming chemical dissociation.

In the next place, Tammann[64] found that zinc even in amalgams as weak as 0.2 per cent lowers the freezing point of the mercury by a deficient amount, not exceeding nine-tenths of the theoretical value—which indicates that the normal fully dissociated condition had not been attained.

Again, Ramsay found an atomic weight of dissolved zinc even at 260°, which was certainly not less than the true value (the average of three determinations was 65.9).

Finally, further evidence showing that zinc is more inclined to double its atoms in mercurial solution than cadmium may be obtained by comparing the volume changes occurring when a gram-atom of zinc or of cadmium is dissolved in varying amounts of mercury. These changes are easily found from the data given on page 14 as follows:

(1) *Zinc Amalgams.*

Amalgam.	Per cent of dissolved metal.	Observed density.	Volume of factors in cell, calculated.	Volume of products in cell, calculated.	Contraction in cell, calculated.
1	0.821	13.472	593.2	591.9	1.3
2	0.733	13.482	663.2	661.8	1.4
3	0.644	13.493	754.2	752.7	1.5
4	0.180	13.530	2686.9	2685.3	1.6

(2) *Cadmium Amalgams.*

5	2.97	13.370	284.2	283.0	1.2
4	2.30	13.405	352.0	350.6	1.4
2	0.74	13.503	1126.2	1124.8	1.4
3	0.37	13.527	2247.6	2246.2	1.4

[64] Zeit. Phys. Chem., 3, 441 (1889).

The atomic volumes of zinc and cadmium were taken as respectively 9.5 and 13.0 in making these calculations.

Thus in both cases the system suffers contraction when the amalgamation takes place. The striking point is that zinc amalgams continue to contract when diluted, showing apparently that molecular rearrangement is still in progress. The contraction of cadmium, however, does not increase so greatly, a sign that the monatomic condition prevails more nearly in concentrated amalgams of this metal.

None of these results is accurate enough to form the basis of exact quantitative calculation, but all point in the same direction. When more accurate measurements of the osmotic pressure have been made, further productive speculation concerning the extent of this strongly indicated partial association of zinc in concentrated amalgams will be possible.

THE APPLICATION OF THE GAS LAW AT INFINITE DILUTION.

It is interesting to note that whatever may be the cause of the superposed effects, the sum total of irregularities in the case of zinc and cadmium diminishes in each case at about the same rate as dilution proceeds. The following table gives the values of the difference between the observed potentials and those demanded by the gas law, when various amalgams of zinc and cadmium are compared with the extrapolated value for infinite dilution. These values are taken from the curves given on pages 45 and 49.

Concentration in gram atoms per liter.	Difference between observed potential of cells and that calculated from gas law.	
	Zinc.	Cadmium.
	Volt.	*Volt.*
[0.00]	— [0.00000]	+ [0.00000]
0.03	— 0.00002	+ 0.00001
0.06	— 0.00004	+ 0.00002
0.12	— 0.00009	+ 0.00004
0.23	— 0.00019	+ 0.00007
0.47	— 0.00041	+ 0.00011
0.93	— 0.00084	+ 0.00018
1.87	— 0.00168	+ 0.00033

Evidently the doubling of the concentration in each case produces a nearly double amount of the irregularity; hence the curves are very similar in shape. The results are advantageously depicted together in figure 10.

This diagram illustrates in a striking manner the most definite and perhaps the most important outcome of the research, namely, the fact that each

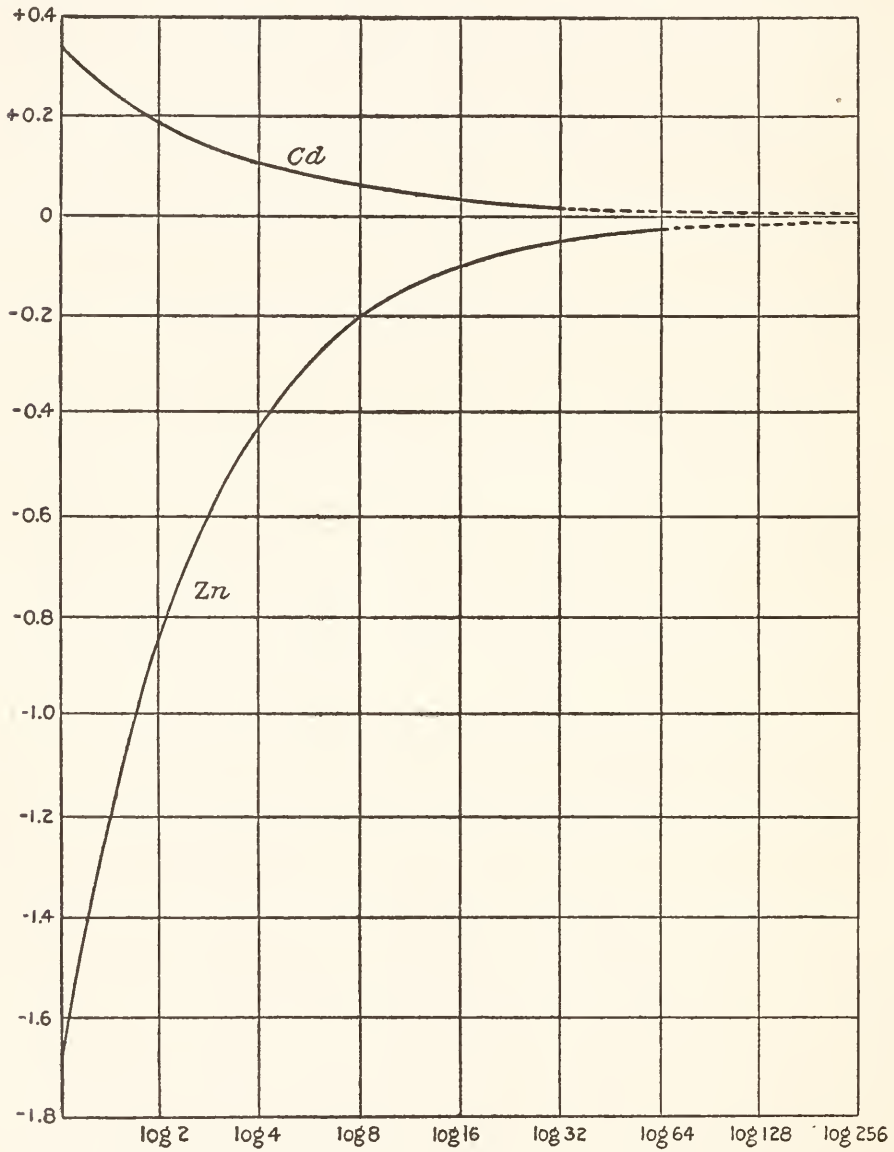

FIG. 10.—THE APPROACH OF THE POTENTIALS OF AMALGAM CELLS TO THE GAS LAW.

Deviations are plotted in millivolts as ordinates; concentration-ratios as abscissæ. The most concentrated amalgams contain each 1.87 gram-atoms per liter. The dotted lines are extrapolated.

amalgam approaches the theoretical value required by the gas law more and more closely as dilution proceeds. The further fact that one of these series of results approaches the limiting value from below and the other from above increases the probability that the gas law holds perfectly in solutions of infinitesimal concentration. From the lower side we have approached the ideal value within 0.3 per cent, from the upper side within 0.2 per cent, and have seen that further dilution would undoubtedly yield yet closer results. The osmotic pressure of zinc or cadmium in the most dilute amalgams investigated was about one atmosphere; it is interesting to note that the irregularities in $p\ v$ existing here appear scarcely greater than those of oxygen and hydrogen gases, whose molal volumes are 22.39 and 22.44 liters, respectively, under normal conditions. This outcome seems to be inconsistent with the idea that the hypothetical bulk of the molecules of solvent affects the osmotic pressure.

Without doubt the present research thus gives the most rigid experimental proof of the exactness of the gas law in dilute mercurial solutions ever obtained. Whether so close an approach has ever been noted in other solvents is doubtful.

In concluding this somewhat lengthy and troublesome investigation, it is a pleasure to acknowledge the important pecuniary aid generously granted by the Carnegie Institution of Washington. This support materially facilitated the work.

SUMMARY.

The main points of the present research may be summarized as follows:

1. The potentials between various liquid amalgams were investigated at 23° C. Extraordinary precautions were taken against experimental errors, and the misuse of absolute units. The results are reliable within 0.00001 volt.

2. Zinc amalgams gave potentials lower than those calculated from the gas law; and cadmium amalgams gave potentials higher than those calculated from the gas law. The regular and symmetrical curves thus constructed show the close approach of these deviations to zero as the dilution is increased.

3. In the most dilute amalgams investigated the closest approach to the gas law ever noted in the study of solutions was found.

4. The temperature-coefficient of the potential of the cadmium amalgam cell was shown to be almost exactly identical with the tension increments of a perfect gas, and that of the concentrated zinc amalgam cell about 3 per cent greater.

5. The heats of dilution of the amalgams were measured directly by a new and accurate calorimetric process, and the results, taken in connection with the temperature-coefficient of the potential, afford a striking verification of the Helmholtz equation.

6. On the other hand, the formula of Cady is found to be inadequate to explain exactly the deviations from the gas law. In no case does the correction indicated by this formula account for more than a small part of the deviations of potential. Therefore, Cady's equation is incomplete. The uncertainty is shown to consist probably in the method of evaluating the volumes to be used in the calculation.

7. The densities of liquid zinc and cadmium amalgams were carefully measured, and the extent of the contraction which takes place on mixing was computed in each case.

8. The constitution of zinc and cadmium amalgams is discussed from chemical and kinetic standpoints. The irregularities of zinc cells are traced primarily to partial polymerization, those of cadmium cells mainly to abnormal osmotic pressures. The situation is shown to be too complex for the complete quantitative treatment of these different tendencies until further results upon osmotic pressure have been obtained.

THE CHEMICAL LABORATORY OF HARVARD COLLEGE,
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Energy Changes Involved in the Dilution of Zinc and Cadmium Amalgams

BY

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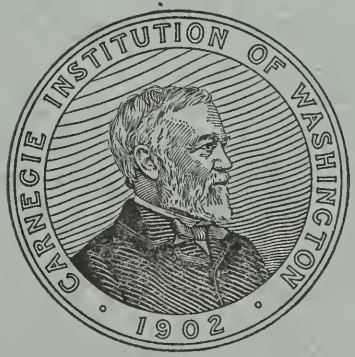

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